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**SOLVENT EFFECTS
ON THE TIME CONSTANT OF POLYMER SOLUTIONS**

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In Partial Fulfilment of the Requirements
for the Degree of
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By
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LOVING MEMORY OF

LATE FATHER AND GRAND FATHER

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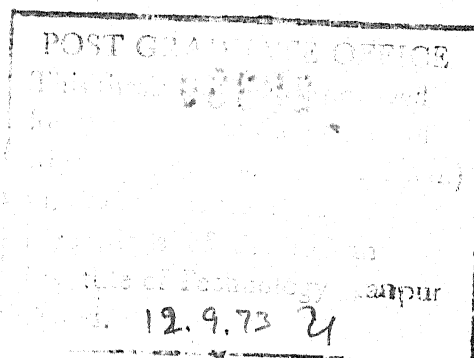
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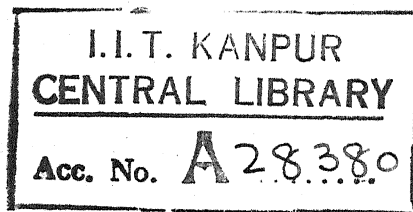
CERTIFICATE

This is to certify that the thesis entitled
"SOLVENT EFFECTS ON THE TIME CONSTANT OF POLYMER SOLUTIONS"
by V.Govardhan Rao for the award of the Degree of Master
of Technology, of Indian Institute of Technology, Kanpur
is a record of bonafide research work carried out by him
under my supervision and guidance. The results embodied
in this thesis have not been submitted elsewhere for a
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TABLE OF CONTENTS

		<u>Page</u>
	Nomenclature	(v)
	Abstract	(vii)
CHAPTER 1	INTRODUCTION	1
CHAPTER 2	LITERATURE SURVEY	5
CHAPTER 3	EXPERIMENTAL WORK	
	Fractionation	11
	Characterization of Polymer Samples	14
	Test Materials	16
	Viscometry	17
CHAPTER 4	RESULTS AND DISCUSSION	
	Description of the Results	19
	Calculation of Experimental Relaxation Time	20
	Superposition of Experimental Curves on a Reference Experimental Curve	21
	Superposition on Williams Theoretical Master Curve	22
	Discussion of the Results	
	Effect of Solvent Character on Viscosity	22
	Functional Dependence of λ on cM	25
	Effect of Solvent Character on Time Constant	26
CHAPTER 5	CONCLUSIONS	29
	Suggestions for Future Work	30
	GRAPHS	31-46
	APPENDIX	47
	REFERENCES	48

NOMENCLATURE

- η , Apparent viscosity, Poise
 η_0 , Zero-shear viscosity, Poise
 η , Upper Newtonian Viscosity, Poise
 $[\eta]$, Intrinsic viscosity, cc/g
 η_s , Solvent viscosity, Poise
 $\dot{\gamma}$, Shear rate, sec^{-1}
 $\dot{\gamma}_R$, Reduced shear rate
 λ , Relaxation time (or time constant), sec.
 $\lambda_B, \lambda_{\text{Bueche}}$, Relaxation time referred to Bueche's theory
 λ_{Rouse} , Rouse relaxation time
 $\lambda_{\text{exp}}, \dot{\gamma}_c$ Time constant and shear rate respectively referred to any of the experimental curve
 $\lambda_r, \dot{\gamma}_r$ Time constant and shear rate respectively referred to reference experimental curve
 A , Shift factor
 M_t , Torque developed by the fluid dyn-cm
 ω , Angular velocity, radians/sec.
 τ , Shear stress, dyn/cm^2
 T , Temperature
 M , Molecular weight
 M_v , Viscosity average molecular weight
 c , Concentration, g/cc
 R , Gas constant

DST, Dilute Solution Theory

CST, Concentrated Solution Theory

PMMA, Polymethylmethacrylate

CB , Chlorobenzene

X , m-xylene

t_o, t_s , Times of efflux of solution and solvent respectively.

ABSTRACT

The viscosity of polymethylmethacrylate as a function of shear rate was studied in chlorobenzene (good solvent) and in m-xylene (poor solvent), using coaxial cylinder viscometer. The molecular weights of polymer studied were, $M_v = 1.340 \times 10^6$ and 2.385×10^6 , the polymer concentrations ranged from 2 to 11 g/dl. All experimental curves are superposed on Williams theoretical master curve and time constants, λ_{exp} for each solution were evaluated. Time constants, assuming dilute solution theories were applicable, λ_{dil} , were calculated from Rouse theory. $\lambda_{\text{exp}}/\lambda_{\text{dil}}$, when plotted against cM , approximately exhibits the functional dependence of $1/cM$ to both good and poor solvent. Williams theoretical relaxation time dependence on $F(c)$, $(\lambda \sim \frac{\eta_0}{c^2 T F(c)})$ where $F(c)$ is a weak function of concentration and solvent character, was not observed experimentally. Instead, the results show that $\lambda_{\text{exp}} \sim \frac{\lambda_{\text{Rouse}}}{cM} \sim \frac{\eta_0}{c^2 T}$, approximately. It was concluded that for the concentrated solutions studied, solvent character influences the relaxation time through zero-shear viscosity, η_0 , which in turn is strongly affected by the solvent character. It also appears that the solvent character at lower concentrations can explicitly influence λ .

CHAPTER 1

INTRODUCTION

The apparent viscosity (η) of polymer melts and their solutions as a function of shear rate ($\dot{\gamma}$) has been studied extensively during past several years. For most systems the dependence of viscosity coefficient on shear rate is an interesting phenomenon. At sufficiently low shear rates, the viscosity coefficient is independent of shear rate and the corresponding viscosity is called zero-shear viscosity (η_0) or the initial Newtonian viscosity. As the shear rate is increased, η decreases with increasing shear rate. Such behavior is termed as non-Newtonian in contrast to the behavior of Newtonian fluids for whom the viscosity coefficient is independent of shear rate. Further increase in shear rate causes the viscosity coefficient to level off and remain constant. Such constant value of viscosity coefficient at high shear rates is called upper Newtonian viscosity (η_∞).

The apparent viscosity of a polymer solution is found to be a complex function of temperature, T , molecular weight, M , mass concentration per unit volume, c , structure of the polymer and character of the solvent. It has been usually assumed that the effect of solvent on rheology of concentrated

polymer solutions is unimportant because of the obvious dominance of entanglements in these systems. However, Gandhi and Williams (1) observed that the influence of solvent character is considerable on zero-shear viscosity by studying moderately concentrated solutions of polymer in a good-solvent and a poor-solvent. Contrary to the usual assumption the effect was found to be more pronounced at higher concentrations. Moreover Tager et.al. (2) qualitatively demonstrated the marked differences in non-Newtonian character observed for good-solvent and poor-solvent systems. Williams (3) theoretically predicted that the character of the solvent should influence the non-Newtonian behavior of polymer solutions. In view of this evidence, it appears that solvent character is no more an insignificant variable.

The onset of non-Newtonian behavior is typically characterized by the time constant, λ . Time constant is approximately equal to the reciprocal of the critical shear rate where the apparent viscosity becomes dependent upon shear rate. Moreover it is usually observed that a non-dimensional plot of η / η_0 vs. $\lambda \dot{\gamma}$ gives a single master curve over a wide range of concentration and molecular weight. The importance of the time constant is apparent from the above observations.

Theoretically Bucche (4) and Rouse (5) developed expressions for time constant for dilute solutions which

differ only by a factor of two.

$$\lambda_{\text{Bueche}} = \frac{12 (\eta_o - \eta_s) M}{\pi^2 c RT} = 2 \lambda_{\text{Rouse}} \quad (1.1)$$

Later on Bueche extended his calculation to melts by letting $\eta_s = 0$ and changing c to melt density. The expressions for melts and dilute solutions were experimentally confirmed. While partially complete investigations of the effect of concentration, molecular weight on the time constant for concentrated polymer solutions were made, the effect of solvent on the time constant has been entirely left out.

The sparsely reported data in literature for concentrated polymer solutions was inconsistent. with Bueche's as well as Rouse's theory, with respect to concentration and molecular weight effects. Williams (3) developed a theory for concentrated solutions which predicts time constant as

$$\lambda \propto \frac{\eta_0 - \eta_s}{c^2 T F(c)} \quad (1.2)$$

which seems to agree with the few existing experimental data. In equation (1.2), $F(c)$ reflects the effect of solvent character.

Before definite conclusions can be drawn regarding the time constant for concentrated solutions more data is needed. The influence of solvent character which was totally left out needs to be studied for concentrated polymer solutions. The present study has been directed in this direction. Commonly available polymethylmethacrylate was selected as the polymer to be studied.

CHAPTER 2

LITERATURE SURVEY

A number of successful developments have been made in the treatment of rheological response based upon the mathematical models of the structure and dynamics of the long chain molecules (3,4,5). The molecular theories proposed by Bueche (4) and by Rouse (5) are for dilute solutions and model the polymer molecule as a collection of mass points connected by springs. Bueche's theory was also extended to polymer melts. Bueche's theory takes the form as

$$\frac{\eta - \eta_s}{\eta_o - \eta_s} = 1 - \frac{6}{\pi^2} \sum_{n=1}^N \frac{(\dot{\gamma} \lambda_B)^2}{n^2 (n^4 + \dot{\gamma}^2 \lambda_B^2)} \left(2 - \frac{(\dot{\gamma} \lambda_B)^2}{n^4 + \dot{\gamma}^2 \lambda_B^2} \right) \quad (2.1)$$

where the parameter λ_B is a relaxation time (or time constant), and is given by Bueche's analysis to be

$$\lambda_B = \frac{12 (\eta_o - \eta_s) M}{\pi^2 c RT} \quad (2.2)$$

The analysis can also be extended, in an adhoc fashion, to the polymer melts with solvent viscosity η_s set equal to zero and with c replaced by polymer melt density, ρ . Rouse theory does not predict non-Newtonian behavior but gives an expression for the longest relaxation time of the polymer molecule as

$$\lambda_{\text{Rouse}} = \frac{6 (\eta_o - \eta_s) M}{\pi^2 c RT} \quad (2.3)$$

As can be seen λ_B and λ_{Rouse} differ by a factor of two. All dilute solution theories, (DST) assume that inter-polymer interactions are unimportant. The numerical magnitude of the predicted value of λ differs from model to model but the dependence of λ on η_o , M and c is always the same and fixed by dilute solution limitation (see Table 1).

The dilute solution theories correlate the data for dilute polymer solutions (9,10,11,12,13) in θ solvents and for polymer melts also (14, 15) surprisingly quite well. Discrepancies with the theory in regard to the shape of the $\log \eta$ vs $\log \dot{\gamma}$ curve were observed due to the broad molecular weight distribution in the polymer sample (16,17,18,19), as well as due to solvent effects in the infinite dilution limit (26). It was also observed that for the low molecular weight samples the relaxation time was proportional to $\frac{\eta_o M}{T}$, devoid of the dependence on concentration in contrast with the theoretical prediction indicating inverse proportionality with concentration. Some average molecular weight like M_v , which would minimize the deviation between theory and experiment, was also recommended (20) and used (13) for Bueche's theory.

It is usually observed that while theoretical prediction based on dilute solution theories of η as a

function of c and M break down at relatively low concentrations, the predictions of λ as a function of c and M work almost till moderately high concentrations. Thus it appears that concentration affects the time constant primarily through the concentration dependence of η_0 , which in the concentration range usually studied, is of the order of c^3 to c^5 . Thus it has become customary to produce master curves of $\log \frac{\eta}{\eta_0}$ vs. $\log \dot{\gamma}$ by superposition on one reference curve by using the reduced shear rate $\dot{\gamma}_R = \frac{\eta_0 M}{c} \frac{c^*}{\eta^*_{M^*}} \dot{\gamma}$ where the starred quantities refer to the reference curve (23). The reduced shear rate should be $\lambda \dot{\gamma}$ and the above expression reflects the fact that $\lambda \propto \frac{\eta_0 M}{c}$. However, there now seems to be enough evidence to show that this would not hold for more concentrated solutions.

DeWitt et al (21) studied solutions of polyisobutylene in decalin over a concentration range of 3-20% and tried to superpose the data with the usual reduced shear rate plots without success. The curves at low concentration superposed, but at higher concentrations tended to be displaced in the direction of higher shear rates. These workers replaced the c in the reduced shear rate by an unknown function of concentration, $f(c)$, which was determined empirically from the shift required to bring the curves into coincidence. The superposition was satisfactory using $f(c) = c$ upto 8% concentration and $f(c) = c^2$ above 8% concentration in the

reduced plots. The observation made by DeWitt et al and similar observations made by others (24, 25) indicates clearly the failure of DST for concentrated polymer solutions.

Williams molecular theory (3) for concentrated polymer solutions as of the form

$$\frac{\eta - \eta_s}{\eta_o - \eta_s} = 1 - \frac{9}{14} \lambda^2 \dot{\gamma}^2 \text{-----} \quad (2.4)$$

The time constant λ , is given as

$$\lambda \sim \frac{(\eta_o - \eta_s)}{c^2 T F(c)} \quad (2.5)$$

where $F(c)$ is a weak function of c and depends on solvent character also. In contrast to DST this concentrated solution theory (CST) is based on the approximation that the effects of intramolecular interactions are negligible compared to the intermolecular interactions. It however does not take entanglements into account. The time constants of the two theories (DST and CST) are given in Table I. The difference in the dependence of λ on molecular weight between CST and DST also is to be taken note of.

Graessley and coworkers (22) obtained non-Newtonian viscosity data on monodisperse polystyrene in n-butyl benzene, covering the range of concentration from 20-55% and molecular weight from 97,200 to 2.4×10^6 . Plots of $\log \frac{\eta(\dot{\gamma})}{\eta_o}$ versus $\log \dot{\gamma}$ were shifted along the $\log \dot{\gamma}$ axis until coincidence with a master curve predicted according to the entanglement

theory was achieved. From the amount of shift needed for each curve for coincidence, relaxation time for that fluid λ_{exp} was calculated. The superposition of these data was good, verifying that a single mechanism of molecular response was dominant. A critical test was made by computing $\lambda_{\text{exp}}/\lambda_{\text{dil}}$, where λ_{dil} was chosen for convenience to be the Rouse value. The ratio should be a constant over a range of c

Table 1

Theory	Prediction
Dilute solution theory	$\lambda_{\text{dil}} \sim K_{\text{dil}} \left[\frac{M(\eta_o - \eta_s)}{cT} \right]$
Concentrated solution theory	$\lambda_{\text{conc}} \sim K_{\text{conc}} \left[\frac{\eta_o - \eta_s}{c^2 T F(c)} \right]$
$\frac{\lambda_{\text{conc}}}{\lambda_{\text{dil}}} = \frac{K}{cM F(c)} \approx \frac{K}{cM}$	

and M if any DST applies and equal to $K/cM F(c) \approx K/cM$ if CST applies (See Table 1). A plot of $\lambda_{\text{exp}}/\lambda_{\text{dil}}$ vs cM is presented in Fig. 14, where it is seen to exhibit distinctly non-DST behavior. However the function is not quite hyperbolic, as is suggested by CST, but only approximately so. Thus neither CST nor DST is satisfactory for concentrated solutions. Graessley et.al.(22) also found that temperature changes do not produce changes in $\lambda_{\text{exp}}/\lambda_{\text{Rouse}}$.

Though ample evidence was developed that the solvent character is no more an insignificant parameter even in concentrated polymer solutions, no work has yet been carried out till now to find out the effect of solvent character on the time constant. Present work dealt with this aspect.

CHAPTER 3

EXPERIMENTAL WORK

(a) Fractionation:

Polymethylmethacrylate (PMMA), was fractionated by means of acetone-hexane precipitation method, following triangular precipitation scheme.

Procedures for separating high polymers into fractions of restricted molecular weight range vary, but all of them depend on the very small decrease in solubility with increase in molecular weight. Fractional precipitation from a dilute solution is the most widely used method. The precipitation is carried out by stepwise decrease in the solvent power of the system. This may be achieved by any of the following methods.

1. Addition of non-solvent (or precipitant)
2. Elimination of solvent by evaporation
3. Lowering the temperature of the system

The first member of the fractions has the highest molecular weight and succeeding ones have progressively decreasing molecular weights.

Even though new chromatographic techniques are rapidly being developed, it is likely that the old fractionation techniques based upon very simple operations will continue

to be popular since the use of elaborate, special and costly equipment is not required. In addition, fractionating methods can be applied to small scale experiments where the molecular weight distribution in small samples is to be examined as well as to the large-scale separation of fractions needed for the study of various properties of high polymers.

Apparatus:

Two "three necked" 5 liter round bottomed flasks were used to process 25 gms of polymer at approximately 1% concentration. Mercury seals were used to prevent evaporation and to provide for stirring the solution vigorously. To make stirrer assembly light, a glass stirrer rod, having a teflon piece as stirrer blade was used.

Materials:

With regard to the selection of the solvent, it is preferable to use a relatively poor solvent so that only a small amount of non-solvent will be required to produce the first fraction, even though it is difficult to dissolve the sample in poor solvent. Relatively weak non-solvent has to be selected so that the amount of polymer to be precipitated can be controlled easily. One further requirement is, to choose a solvent-nonsolvent system which produces an easily handled precipitate. By a process of trial and error, a suitable solvent-nonsolvent pair may be found which

will reduce these difficulties. Cantow (6) lists several suitable solvent-nonsolvent pairs for various polymers.

In this work, PMMA was fractionated using acetone as solvent and hexane as precipitant. PMMA is available under the commercial name, perspex. Perspex sheets were directly used for fractionation since the plasticizer will be carried by either the lowest molecular weight polymer or the solvent-non solvent mixture. Commercial acetone was distilled before use and commercial n-hexane was directly used.

Procedure:

The precipitations were carried out following triangular scheme method. Successive refractionation is necessary to achieve better separations. One such refractionation scheme is the triangular method which is illustrated in Fig. 1. where the horizontal arrows indicate supernatant liquid and downward arrows indicate precipitations. In this method, the precipitant of a fraction at one particular stage is dissolved in the supernatant liquid of the preceding fraction of the next stage and precipitation is carried out. The lowest molecular weight sample is obtained by directly evaporating the supernatant liquid of the last precipitation of the 1st stage. For details see elsewhere (6).

The precipitations were conducted at 40°C. The polymer sample (PMMA) was dissolved in acetone and n-hexane

was added gradually to the solution contained in 5 litre 3 necked round bottomed flask until a slight turbidity developed. At the same time the solution was subjected to vigorous agitation. At this stage dropwise addition of nonsolvent (n-hexane) was added until the solution turned milky. For the purpose of assuring establishment of equilibrium between the two phases which form, the solution was constantly stirred for considerable time. Then the agitation was stopped and the precipitated phase was allowed to settle. After it had formed a coherent layer, which may require 2 to 4 hours, the supernatant phase was decanted into the other 5 litre 3 necked round bottomed flask. The precipitated phase, which contains the fraction consisting of the highest molecular weight species, was collected by dissolving in a small amount of solvent or solution as specified according to the scheme illustrated in Fig.1. The supernatant liquid was treated with further volume of non-solvent using the same procedure described above, to obtain the next fraction.

b. Characterization of the Polymer Samples:

The polymer samples can be characterized by various methods. One such method is based on measurement of intrinsic viscosity. Cannon-Ubbelohde capillary viscometer was used to measure the intrinsic viscosity. In this viscometer, time of efflux of a fixed quantity of fluid through a capillary

is observed. The time of efflux, as long as it is larger than 150 seconds, is directly proportional to viscosity of the solution. Intrinsic viscosity, $[\eta]$, is defined as

$$\lim_{c \rightarrow 0} \frac{\eta_o - \eta_s}{\eta_s c} = [\eta] \quad (3.1)$$

$$\text{Hence } [\eta] = \lim_{c \rightarrow 0} \frac{t_o - t_s}{c t_s} \quad (3.2)$$

The empirical Mark-Houwink relationship between $[\eta]$ and M is

$$[\eta] = K M^a \quad (3.3)$$

K and a are constants determined experimentally. The values of K and a are tabulated extensively in Polymer Handbook (7).

Procedure:

Intrinsic viscosity measurements were carried with toluene as solvent at 25°C. The efflux times of the solvent and solutions at different concentrations were noted. A graph of $(t_o - t_s)/c t_s$ versus concentration was plotted (Fig.3). The intercept at zero concentration gives the intrinsic viscosity. The viscosity average molecular weight was calculated according to the equation (3.3) obtained from Polymer Handbook (7). Table 2 contains the information about the samples used.

Table 2

Solvent	T, °C	$K \times 10^5$ dl/g	a	Polymer	$[\eta]$ dl/g	$M_v \times 10^{-6}$ (From $[\eta] = KM^a$)
Toluene	25	7.1	0.73	PMMA	3.21	2.385
Toluene	25	7.1	0.73	PMMA	2.11	1.340

c. Test Materials:

Polymethylmethacrylate (PMMA) was studied in two different solvents. Chlorobenzene and m-xylene were chosen as solvents due to their low vapor pressure at room temperature which will minimize the evaporation losses. Chlorobenzene is a good solvent and m-xylene is near θ solvent for PMMA. Four combinations of solvent, molecular weight of polymer which were studied are shown in Table 3. Reagent grade solvents were obtained and were used without further purification.

Table 3

Polymer	M_v (from $[\eta] = KM^a$)	Solvents	
		Good	Poor
PMMA	2.385×10^6	Chlorobenzene	m-xylene
PMMA	1.340×10^6	Chlorobenzene	m-xylene

A master solution of PMMA was prepared in chlorobenzene (CB), and m-xylene (X). Known amounts of master solution

and solvent were mixed and heated in a closed container for several days at 70°C. The weight fraction was obtained for each solution by gravimetric analysis. Weight fraction was then converted into mass concentration, c , through density data.

d. Viscometry:

All viscosity measurements were made with a commercial model of a coaxial cylinder (Couette) viscometer, called Rheotest 2, shown in Figure 2. The viscometer is provided with twelve speeds and five different cylinder measuring systems, which are distinguished by their geometrical dimensions. A wide range of shear rates ($0.2 - 1310 \text{ sec}^{-1}$), can be attained and a range of viscosities ($1 - 1.8 \times 10^7 \text{ c P}$) can be measured with this system.

In Rheotest 2, the outer cylinder of radius R is fixed and the inner cylinder with radius r , and length, L , is rotated with constant angular velocity, ω . The following standard relations exist:

$$\tau = \frac{M_t}{2 \pi L r^2} \quad (3.4)$$

$$\dot{\gamma} = \frac{\omega R^2}{R^2 - r^2} \quad (3.5)$$

$$\eta = \tau / \dot{\gamma} \quad (3.6)$$

The calculated parameters τ and $\dot{\gamma}$ are referred to the inner cylinder. For derivations of the above equations, see elsewhere (8). In Rheotest 2, M_t is measured for a given ω and hence η can be calculated. The cylinder measuring systems, with $r/R = 0.98, 0.94$, were employed since for the other systems, available r/R ratio was 0.81. The flow stability was checked at the highest shear rate employed for a given sample. All systems were found to be within the stability region.

CHAPTER 4

RESULTS AND DISCUSSION

Description of Results:

The two samples of PMMA were studied in chlorobenzene (good solvent) and in m-xylene (poor solvent) over 2-11 g/dl concentration range covering a wide range of shear rates ($0.5 - 1312 \text{ sec}^{-1}$). Apparent viscosity (Poise) versus shear rate (sec^{-1}) are plotted on log-log scale for each system and are presented in Figs. 4,5,6 and 7. These plots show the typically observed non-Newtonian behaviour of polymer solutions. The experiments were carried out at 25°C in the case of chlorobenzene and at 35°C in the case of m-xylene. Although it was reported that m-xylene is a θ solvent for PMMA at 25°C , it was found in our laboratory that the polymer precipitated in m-xylene (poor solvent) at 25°C . Hence it was decided that PMMA solutions in m-xylene would be studied at 35°C , which was the minimum temperature at which precipitation did not occur for a period of 2 hours. A plot of zero-shear viscosity versus concentration is presented in Fig. 8. The apparent viscosity is non-dimensionalized dividing by zero-shear viscosity for each concentration and it is plotted against shear rate in Figs. 9,10,11 and 12. Fig. 13 shows the superposition of all curves on a master curve. From the master curve the relaxation time, λ_{exp} for each concentration of different

molecular weights in chlorobenzene and m-xylene is calculated. λ_{exp} are tabulated in Table 4. The ratio of λ_{exp} to Rouse relaxation time (Rouse relaxation time was calculated from equation (2.3)) is plotted against concentration for each molecular weight studied in both good and poor solvent (See Fig. 15).

Calculation of Experimental Relaxation Time:

To determine λ_{exp} , theoretical master curves predicted by Williams, Graessley and Bueche were compared with the shape of each of the experimental curve. The theoretical curves plot \log of η / η_0 versus \log of $(\lambda \dot{\gamma})$ or the \log of reduced shear rate. The selected master curve was superposed upon the experimental curve to provide the best fit, then for any given value of η / η_0 , then the product of shear rate and relaxation time of the experimental curve ($\dot{\gamma}_0 \lambda_{\text{exp}}$) must be equal to the reduced shear rate of the master curve at the same value of η / η_0 . The unknown quantity, λ_{exp} was then calculated. It was observed that none of the theoretical curves were identical in shape with the experimental one throughout the shear rate range. Hence some visual judgement has to be made to arrive at the best fit between the experimental curve and the theoretical curve. However, it was difficult to arrive at the "same kind" of best fit for different curves by visual comparison. As a result, of the values of λ_{exp}

obtained by comparing the experimental curves separately with any of the master curves contained large errors, merely reflecting the inconsistency of visual comparison. Hence the attempt to compare the curves separately on a selected theoretical master curve and to calculate λ_{exp} was abandoned. Instead, one of the experimental curves (the curve corresponding to $M_v = 2.385 \times 10^6$ and $c = 0.0839$ g/cc in chlorobenzene) was chosen as a reference curve and the remaining curves were shifted horizontally (along the $\dot{\gamma}$ axis) until they superposed on the chosen reference curve. The resulting plot is shown in Fig.13 indicating the satisfactory superposition. Even though visual judgement was used in superposition here also, the dependence on the judgement was less severe as the shapes of the curves were quite similar throughout the range of $\dot{\gamma}$ studied. The amount of the shift or shift factor, $\log A$, needed for superposition for each curve was noted. The shift factor is the logarithm of the ratio of the shear rates of the curve being compared and the reference curve at which η / η_0 has the same value. If $\dot{\gamma}_c$ and $\dot{\gamma}_r$ are the two shear rates indicated respectively, then

$$\log A_c = \log \frac{\dot{\gamma}_c}{\dot{\gamma}_r} \quad \text{or} \quad A = \frac{\dot{\gamma}_c}{\dot{\gamma}_r}$$

However a plot of $\log \eta / \eta_0$ versus $\log \lambda \dot{\gamma}$ should give a master curve where all data should superpose on the curve. From this it is clear, therefore, that $\lambda_r \dot{\gamma}_r = \lambda_{\text{exp}} \dot{\gamma}_c$

or $\lambda_{\text{exp}} = \lambda_r/A$. Thus all the values of λ_{exp} are known in terms of λ_r .

The master curve obtained by superposing all curves on the reference curve was then shifted along the $\log \dot{\gamma}$ axis to provide the best fit with Williams theoretical master curve. It is observed that Williams master curve correlates our data at low shear rates well although discrepancy prevails as the shear rates are increased. Graessley's master curve does exactly the opposite (See Fig. 13). The time constant of the reference curve, λ_r , was calculated as already indicated (in the beginning of the section) by comparison with Williams theoretical curves. From λ_r and A , time constants were then evaluated for all the curves. For comparative purposes, the theoretical dilute solution relaxation times were also calculated from Rouse theory. The experimental relaxation times and Rouse relaxation times are tabulated in Table 4.

Discussion of the Results:

The data of the Figures 4,5,6 and 7 demonstrate that the viscosities of the solutions in poor solvent are much higher than the viscosities of the solutions in good solvent throughout the shear rate interval. This is due to the structures formed due to association of polymer molecules in poor solvent. In a poor solvent, the polymer molecule has

TABLE 4

SUMMARY OF FLOW PARAMETERS

$M_v \times 10^{-6}$	c, g/cc	T, °C	Solvent	η_o , Poise	λ_{exp} sec $\times 10^3$	λ_{Rouse} Sec $\times 10^3$
2.385	0.0839	25	Chlorobenzene	116.00	222.00	81.10
"	0.0720	"	"	55.50	127.00	45.20
"	0.0566	"	"	19.25	59.20	19.95
"	0.0356	"	"	2.90	15.35	4.78
"	0.0191	"	"	0.47	2.77	1.43
1.340	0.1100	"	"	42.80	49.40	12.85
"	0.0865	"	"	19.40	23.30	7.40
"	0.0780	"	"	13.40	18.50	5.66
"	0.0574	"	"	3.45	6.24	1.98
"	0.0398	"	"	1.09	2.22	0.90
2.385	0.0492	35	m-xylene	77.50	284.00	89.50
"	0.0365	"	"	18.50	96.5	28.80
"	0.0312	"	"	8.50	52.90	15.50
"	0.0219	"	"	1.60	15.85	4.15
1.340	0.0540	"	"	17.00	34.20	10.04
"	0.0389	"	"	3.52	13.30	2.89
"	0.0358	"	"	2.18	9.25	1.94

relatively low affinity to the solvent and tries to associate with the segments of the neighbouring polymer molecule which ultimately leads to aggregation. This type of aggregation is a localized phenomenon, it depends only on concentration but not on molecular weight as it is thermodynamic in nature. Hence in a poor solvent, a polymer molecule can move only along with other associated polymer molecules which contributes to increased viscosity. However, comparatively, a polymer molecule in a good solvent finds it easier to move among the neighbours because of absence of aggregation. Note that, although entanglements may form at moderately high concentration, it is common to polymer molecules in both the solvents. The $\log \eta_0$ versus concentration is shown in Fig.8 which exhibits the above described significant effect of solvent character on zero shear viscosity and also is in agreement with the previous results (1). It is interesting to note that the effect of solvent is so strong that the zero shear viscosity of the low molecular weight PMMA ($M_v = 1.340 \times 10^6$) in poor solvent eventually surpasses the high molecular weight PMMA ($M_v = 2.385 \times 10^6$) in good solvent as the concentration is increased. Another interesting observation is that the viscosity of polymer in good solvent decreases more rapidly than in poor solvent, as the shear rates are increased (Figs. 4 and 5). Further it is observed with poor solvent that the viscosity well level off at high shear rates Figs.(6,7).

Such behaviour is absent in good solvent. It appears that this behaviour is due to the formation of two kinds of structures in good and poor solvents: the entanglement structures that are deformed under the action of applied stress in good solvent and the slightly swollen super molecular (aggregates) structures that are reversibly disintegrated under the action of applied stress in poor solvent. The aggregative forces are relatively weak because of their physical nature and hence are easier to be broken up as shear stress is increased causing a decrease in viscosity. Thus it appears that as shear stress is increased to a certain value these structures are broken up completely and viscosity remains constant. Deformation of entanglements involves coordination of several bond movements and is relatively more difficult to achieve completion. Thus levelling off does not appear in good solvent. It also appears that non-Newtonian behaviour due to entanglements may be absent in the shear rates studied in poor solvents as the entanglements are relatively tighter due to solvent effects, although only further investigation at higher shear rates can confirm this fact.

Focusing the attention now on λ_{exp} , it was observed that the superposition of our data on Williams master curve is very good at low shear rates, thereafter the theory predicting more non-Newtonian behaviour at high shear rates (as shown in Fig. 13). Comparison of data with Graessley's master curve at

high shear rates is good, but at low shear rates it is far off with the experiment. Since the usefulness of λ lies in predicting the onset of non-Newtonian behaviour, Williams curve was chosen to calculate λ values of our data. The deviation from Williams theory at high shear rates is to be expected since the theory was developed specifically for low shear rates. However, it must be mentioned that deviation from either Williams theory or from Graessley's master curve can be due to the broad (even though relatively small due to fractionation) molecular weight distribution.

The data of Fig. 15 demonstrate that $\lambda_{\text{exp}}/\lambda_{\text{Rouse}}$ is an explicit function of only concentration and molecular weight irrespective of the solvent nature in the range of c and M studied. The data for two different molecular weights are superposed on a single curve when $\lambda_{\text{exp}}/\lambda_{\text{Rouse}}$ is plotted against cM as shown in Fig. 16. Thus it appears that $\lambda_{\text{exp}}/\lambda_{\text{Rouse}}$ is an explicit function of only cM . It is to be noted that Graessley (22) found $\lambda/\lambda_{\text{Rouse}}$ to be a function of cM for varying M and c , but only in one solvent. As observed by Graessley (22) the dependence is not given exactly by $1/cM$. This implies that

$$\frac{\lambda_{\text{exp}}}{\lambda_{\text{Rouse}}} \sim \frac{\eta_0}{c^2 RT}$$

only approximately. Thus Williams theoretical prediction is only approximate.

It is to be expected that, when $\lambda_{\text{exp}}/\lambda_{\text{Rouse}}$ is plotted against cM , the relaxation time ratio should not depend upon cM as $c \rightarrow 0$ if any DST is applicable. Hence it is to be expected that the approximate hyperbolic shape of this curve should cease as $c \rightarrow 0$ and should reach a constant value. If the Rouse theory is applicable, the constant value should be unity and if Bueche's theory is applicable the constant should be equal to 2. Thus it may be expected that as $c \rightarrow 0$ the curve should come down and level off around $\lambda_{\text{exp}}/\lambda_{\text{dil}} = 2$ or 1. The data in Fig. 16 throw some light on the transition region where neither DST nor CST applies. It is interesting to note that at the lower concentrations studied, the functional dependence of $\lambda_{\text{exp}}/\lambda_{\text{Rouse}}$ upon cM has a definite downward trend to both the molecular weight samples in chlorobenzene (good solvent) whereas this behavior is totally absent in poor solvent. Thus it can be concluded that poor solvent makes a polymer solution behave like a more concentrated solution with respect to time constant. This effect is similar to the effect of solvent on η_0 .

All these observations lead to the conclusion that Williams theoretical relaxation time dependence ($\lambda \sim \frac{\eta_0}{c^2 T F(c)}$) on $F(c)$, where $F(c)$ is a weak function of concentration and solvent character, was not observed experimentally at high concentrations where entanglements and or aggregates form. The solvent character influences the relaxation time only

through zero-shear viscosity, η_0 . However it is important to note that η_0 strongly depends on solvent character as already indicated by our data. At low concentrations, one may conclude from our data, even though more work is needed in this region, that the nature of the solvent also might come into the picture explicitly to influence the relaxation time. Although the data in chlorobenzene was taken at 25°C and compared with data in M-xylene which was taken at 35°C this is not expected to effect our conclusions very much. This conclusion is based on Graessley's data (22) on polystyrene in ethylbenzene (a good solvent) who found that $\lambda/\lambda_{\text{Rouse}}$ changed by only 4% when temperature was changed from 30°C to 60°C. Thus $\lambda_{\text{exp}}/\lambda_{\text{Rouse}}$ values for PMMA in chlorobenzene at 25°C and 35°C can be expected to be almost the same.

CHAPTER 5

CONCLUSIONS

Two samples of PMMA, having $M_v = 2.385 \times 10^6$ and 1.340×10^6 were studied in chlorobenzene (good solvent) and in m-xylene (poor solvent) over a concentration range of 2-11 g/dl to estimate the experimental relaxation time and its dependence on molecular weight, concentration and solvent character.

1. The dependence of relaxation time on molecular weight and concentration agrees with others. It was found that $\lambda_{\text{exp}}/\lambda_{\text{Rouse}}$ was only a function of cM and that Williams prediction, $\lambda \sim \frac{\eta_0}{c^2 T}$, is only approximately true.

2. It was observed that the solvent character does not explicitly influence the time constant at high concentrations, but it affects the time constant through its strong dependence on zero shear viscosity. At low concentrations, it seems that the solvent character might be an explicit function of time constant, but more data is needed to conclude anything definitely.

Suggestions for Future Work:

The present work was in a position to analyse the data well at high concentrations. More experimental data in the transition range (range between dilute to concentrated) is needed to explain fully the functional dependence of time constant on the nature of the solvent as solvent effects in this range may be important. Such work needs a high shear rate viscometer which is at present not available at IIT-Kanpur.

- | | |
|----------------------------------|---------------------------------|
| 1 Viscosimeter | 25 Coupling |
| 2 Measuring unit | 26 Sleeve |
| 3 Drive | 27 Clamping ring |
| 4 Measuring head | 28 Clamping lever |
| 5 Cylinder measuring system | 29 Thermometer |
| 6 Base | 30 Clamping ring |
| 7 Change-speed gear | 31 Clamping lever |
| 8 Gear bridge | 47 Switch (motor) |
| 9 Gear-shift lever | 48 Switch(measuring head) |
| 10 Scale | 49 Indicating instrument |
| 11 Speed-change switch | 50 Zero adjustment (mechanical) |
| 12 Measuring shaft | 51 Zero adjustment (electrical) |
| 13 Drive shaft | 52 Frequency meter |
| 14 Dynamometer | |
| 15 Instrument potentiometer | |
| 16 Range lever | |
| 17 Measuring cylinder | |
| 18 Measuring vessel | |
| 19 Temperature regulating vessel | |

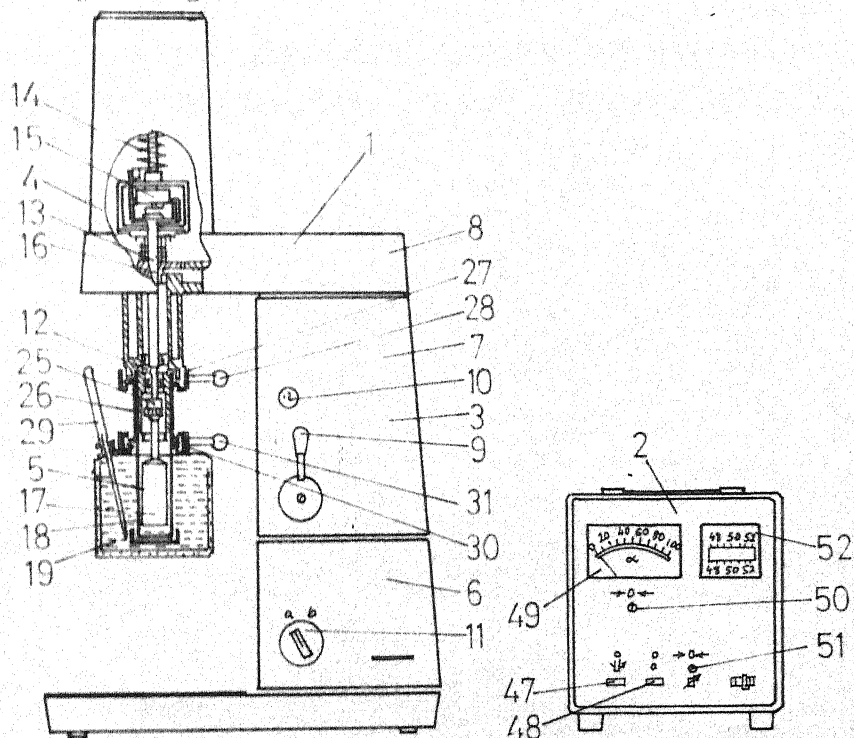


Fig. 2 - Rheotest 2 with cylinder measuring system.

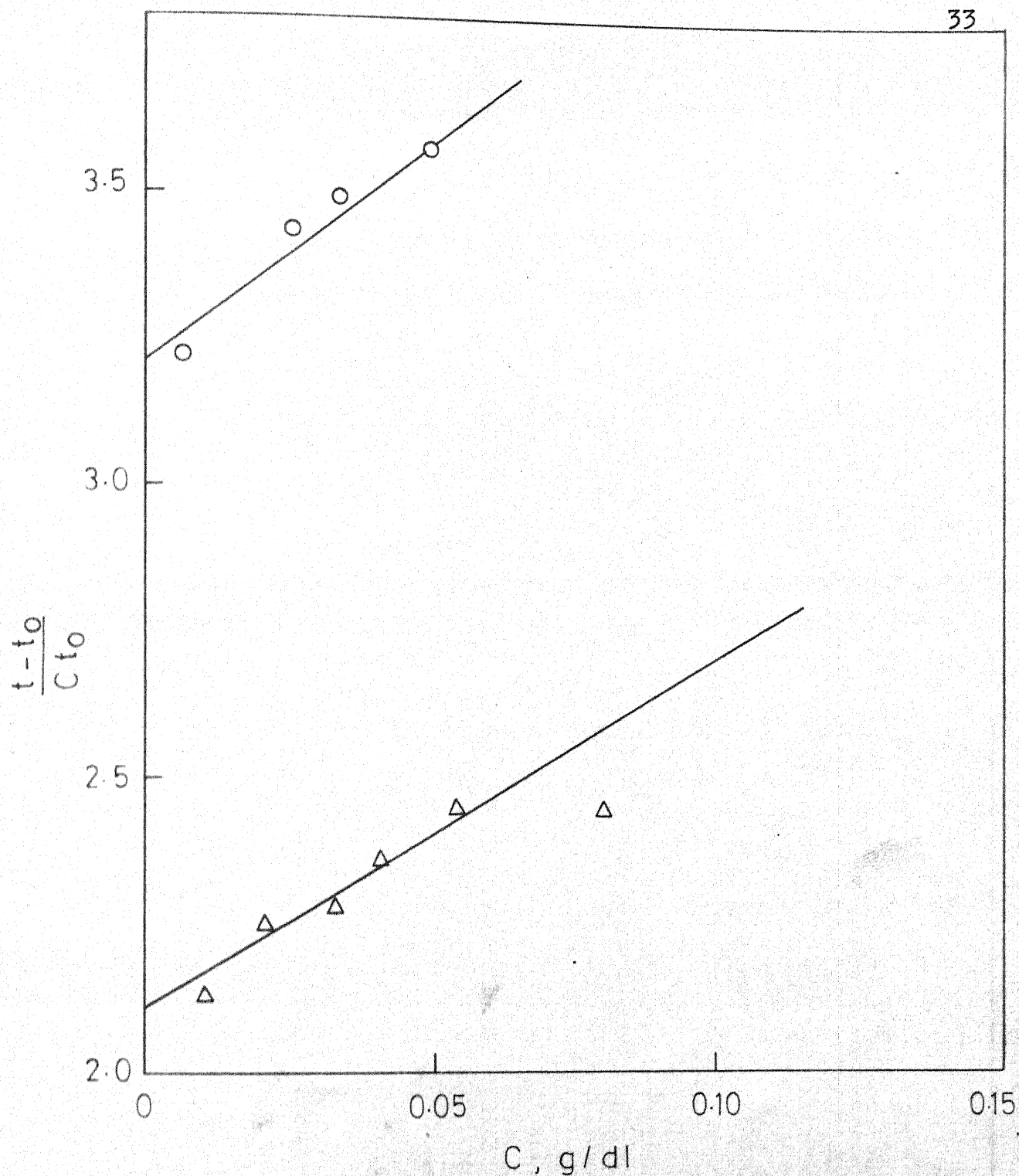


Fig. 3 - C versus $\frac{t-t_0}{Ct_0}$ for two different molecular weights of PMMA. The intercepts of the straight lines as $C \rightarrow 0$ give the intrinsic viscosities. The viscosity average molecular weights were calculated from the equation $[\eta] = KM^a$ (see table 1).

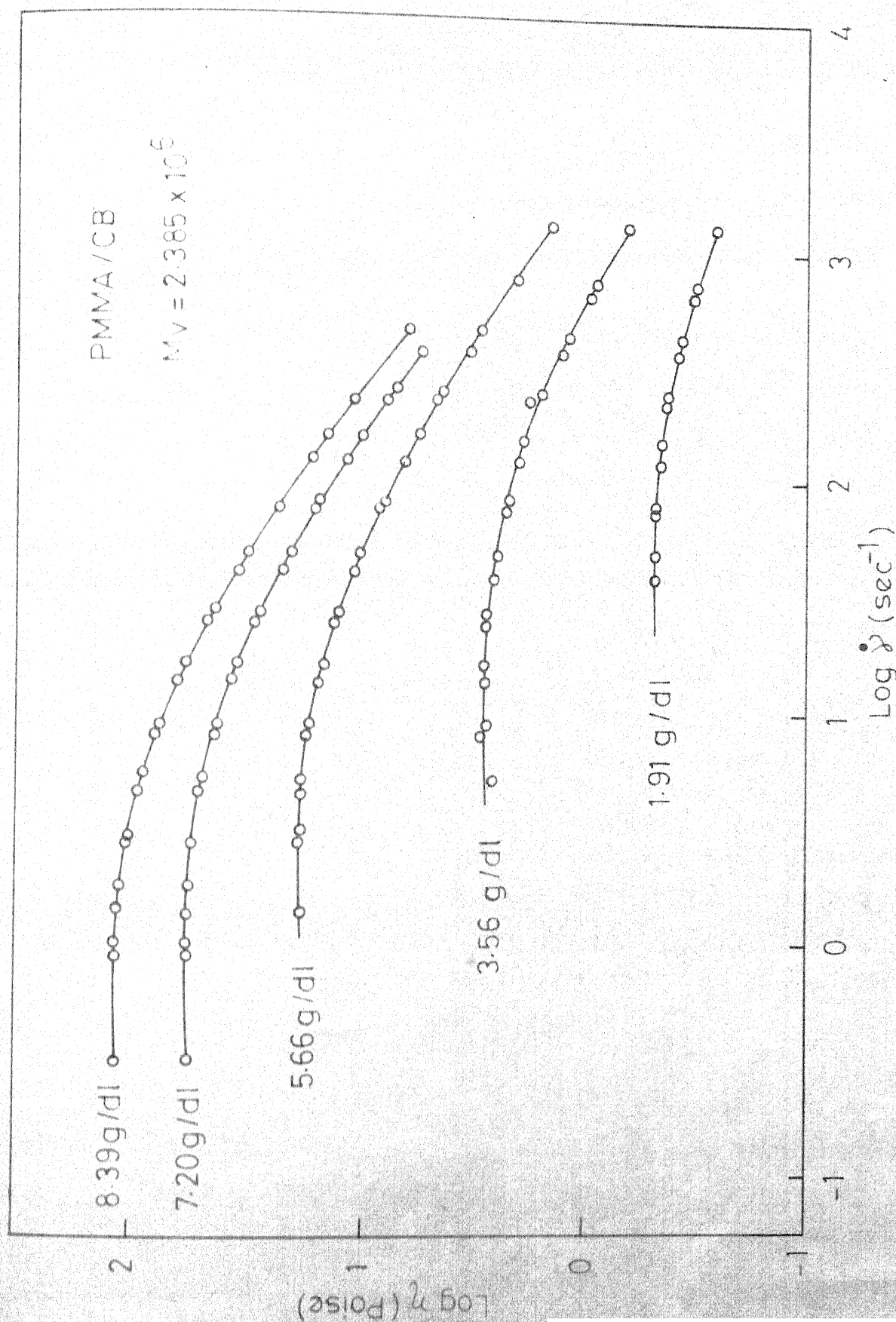


Fig. 4 - Viscosity of polymethylmethacrylate in chlorobenzene (PMMA/CB) for different concentrations. The PMMA was $M_v = 2.385 \times 10^5$ at 25°C . Chlorobenzene is a good solvent for this polymer.

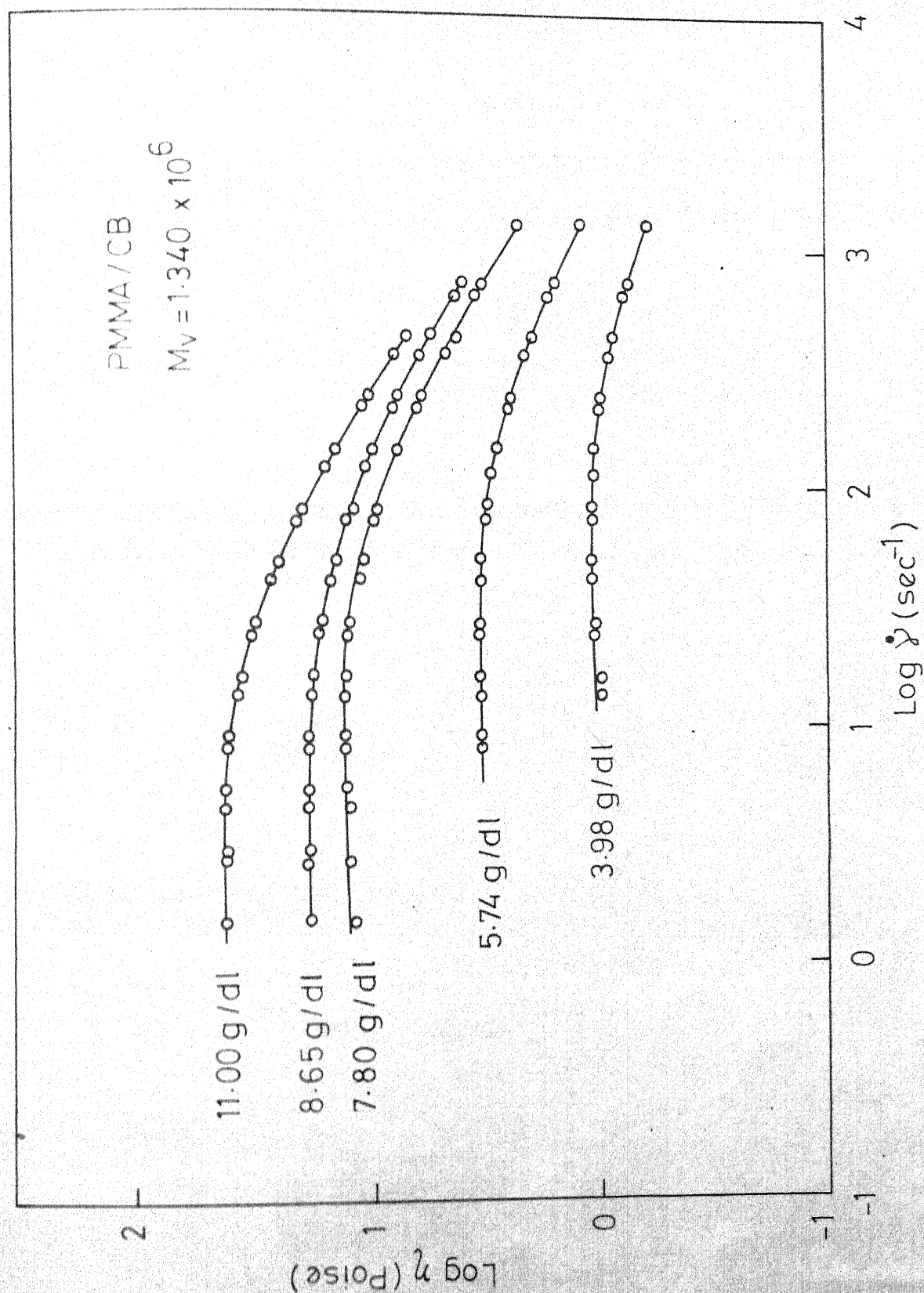


Fig. 5 - Viscosity of polymethylmethacrylate in chlorobenzene (PMMA/CB) for different concentrations. The PMMA was $M_V = 1.340 \times 10^6$ at 25°C . Chlorobenzene is

good solvent for this polymer.

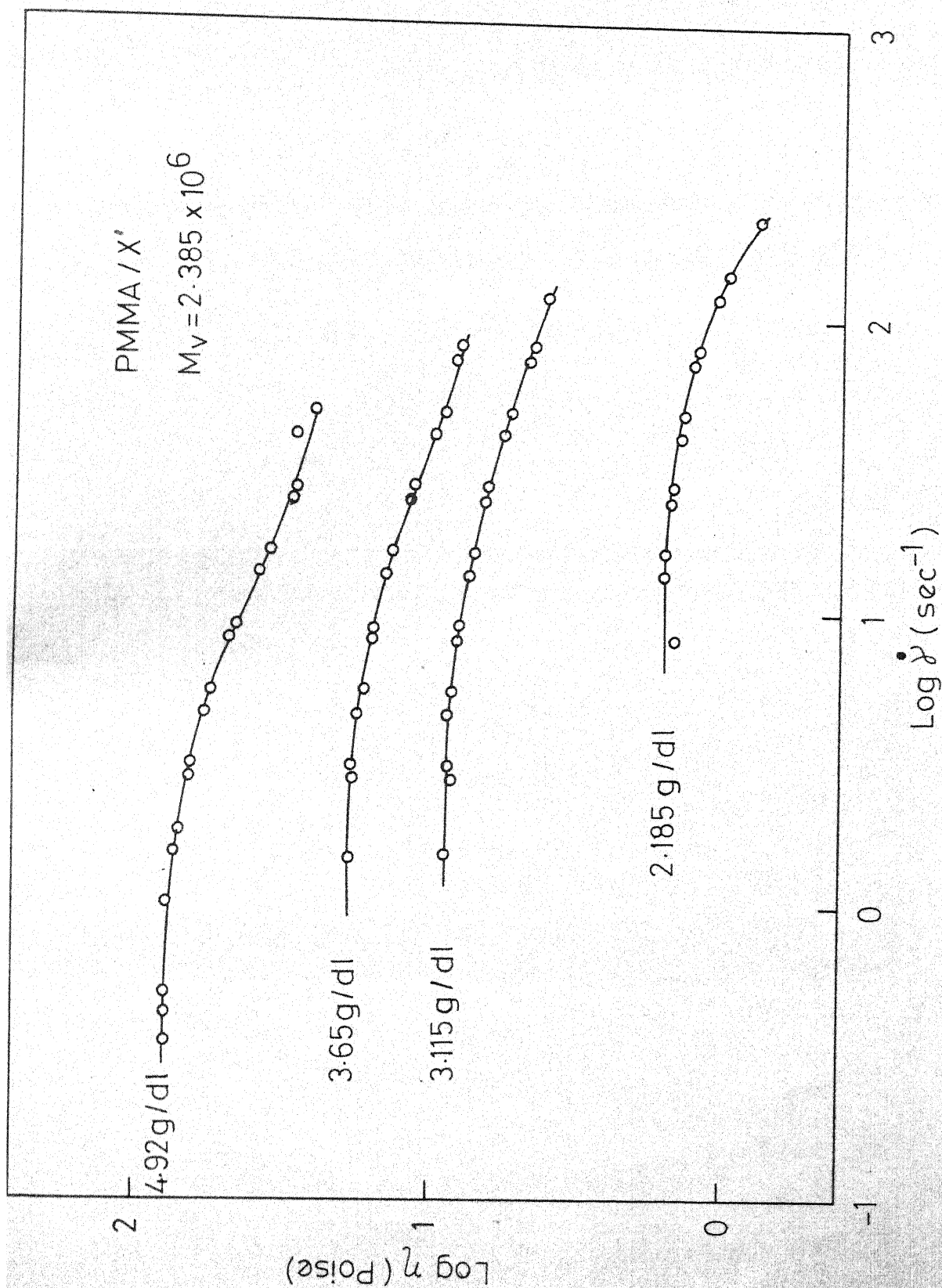


Fig. 6 - Viscosity of polymethylmethacrylate in m-Xylene (PMMA/X) for different concentrations. The PMMA was $M_V = 2.385 \times 10^6$ at 35°C. m-Xylene is a poor solvent for this polymer.

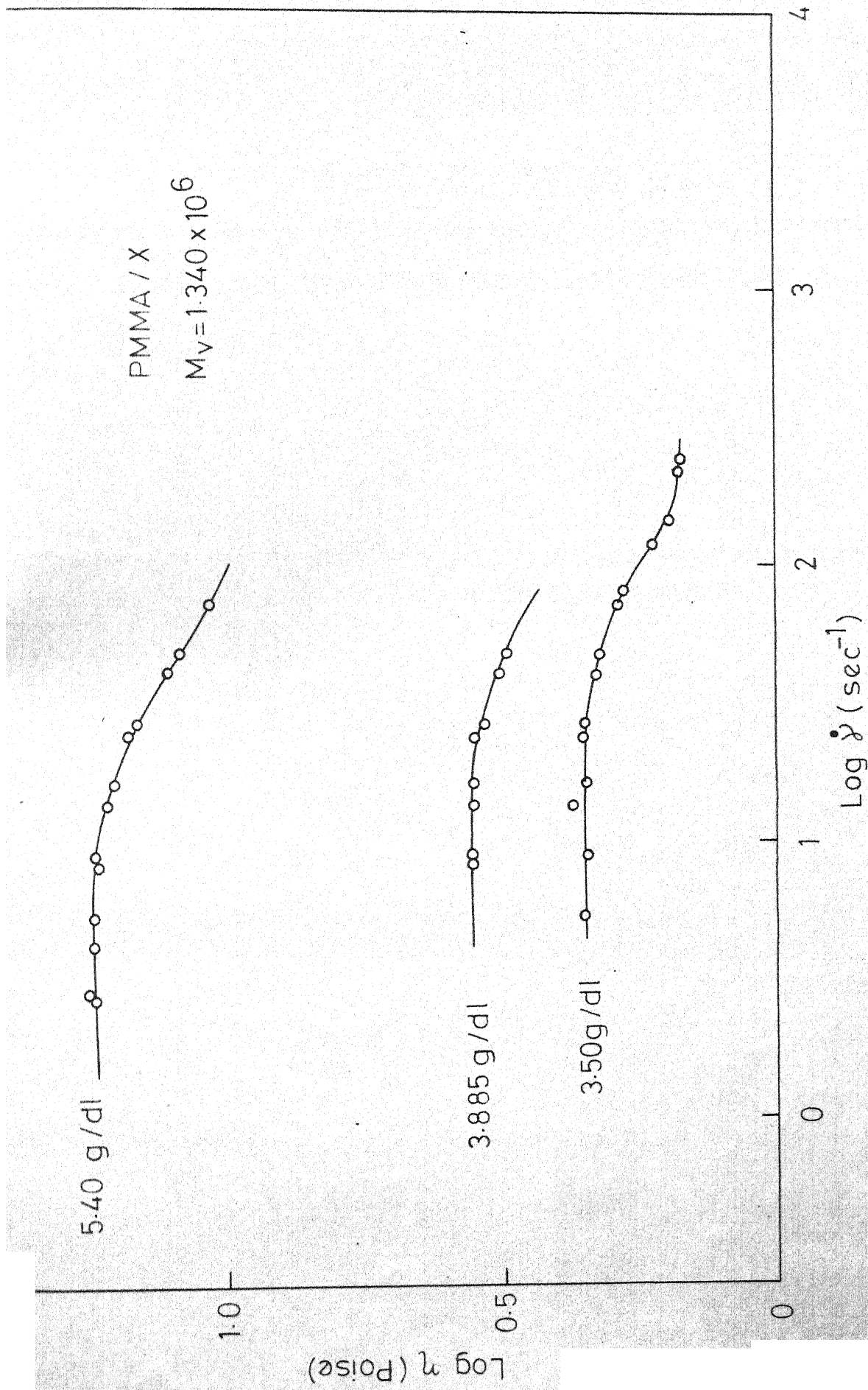


Fig. 7 - Viscosity of Polymethylmethacrylate in m-Xylene (PMMA/X) for different concentrations.

The PMMA was $M_V = 1.340 \times 10^6$ at 35°C. m-Xylene is a poor solvent for this polymer

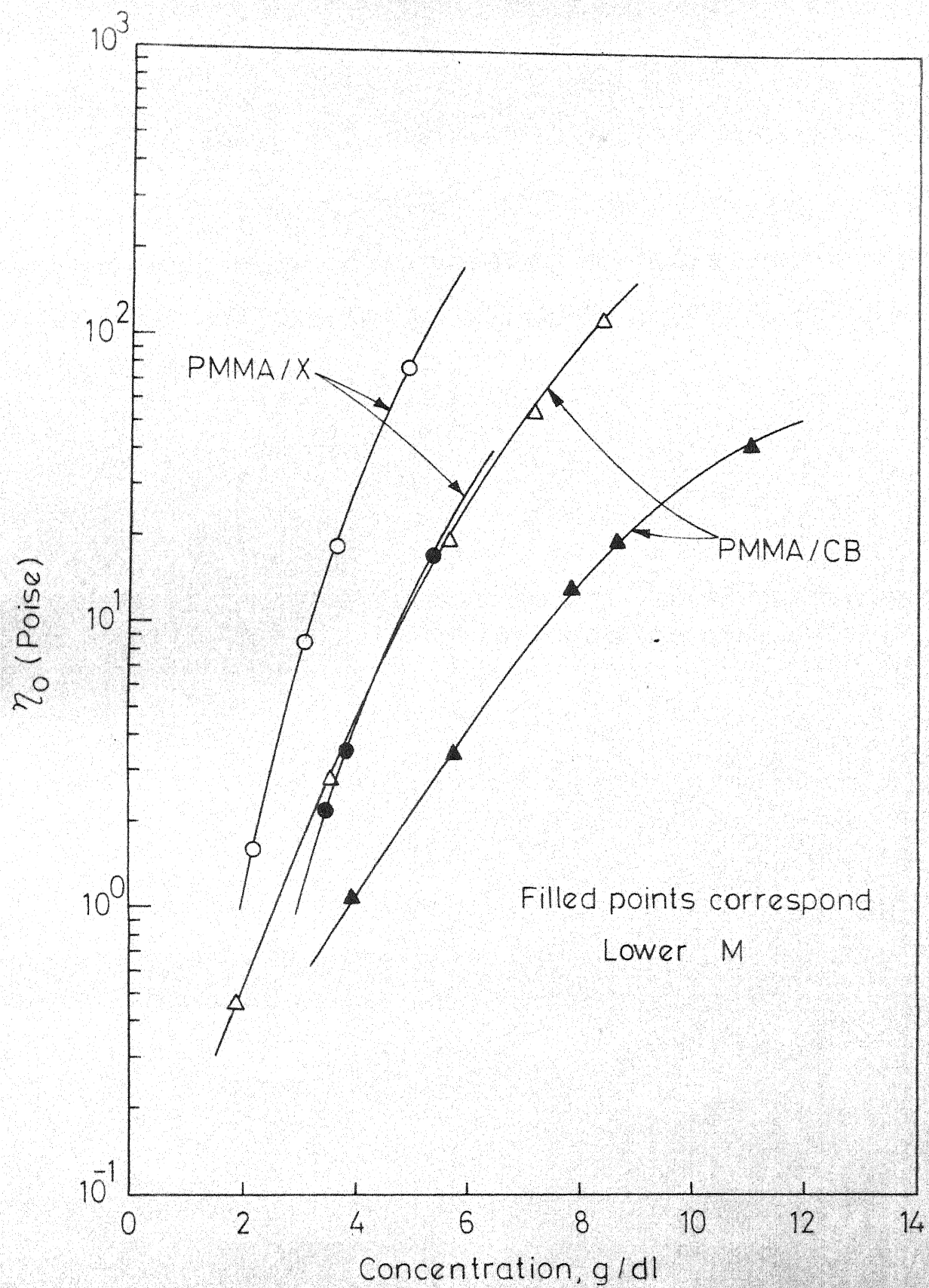


Fig. 8 - Zero shear viscosity of PMMA in chlorobenzene (Good solvent) and in m-Xylene (Poor solvent) at 25°C and 35°C respectively.

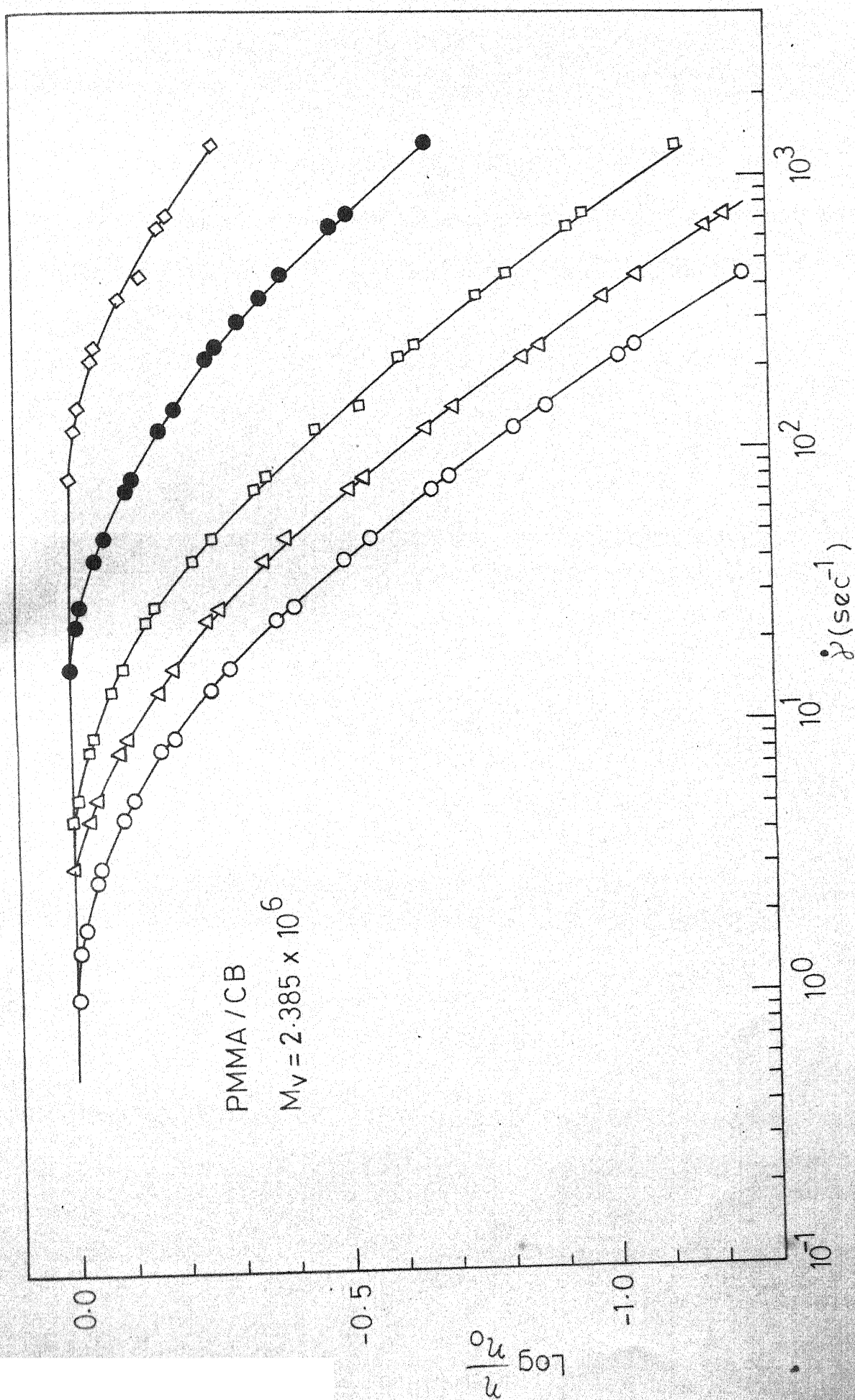


Fig. 9 - Log $\frac{\eta}{\eta_0}$ versus $\dot{\gamma}$ for polymethylmethacrylate in Chlorobenzene (PMMA / CB) at 25°C. Chlorobenzene is a good solvent for this polymer: $M_V = 2.385 \times 10^6$; The points represent different concentrations: (○) 8.39 g/dl; (Δ) 7.20 g/dl; (□) 5.66 g/dl; (●) 3.56 g/dl; (◇) 1.91 g/dl.

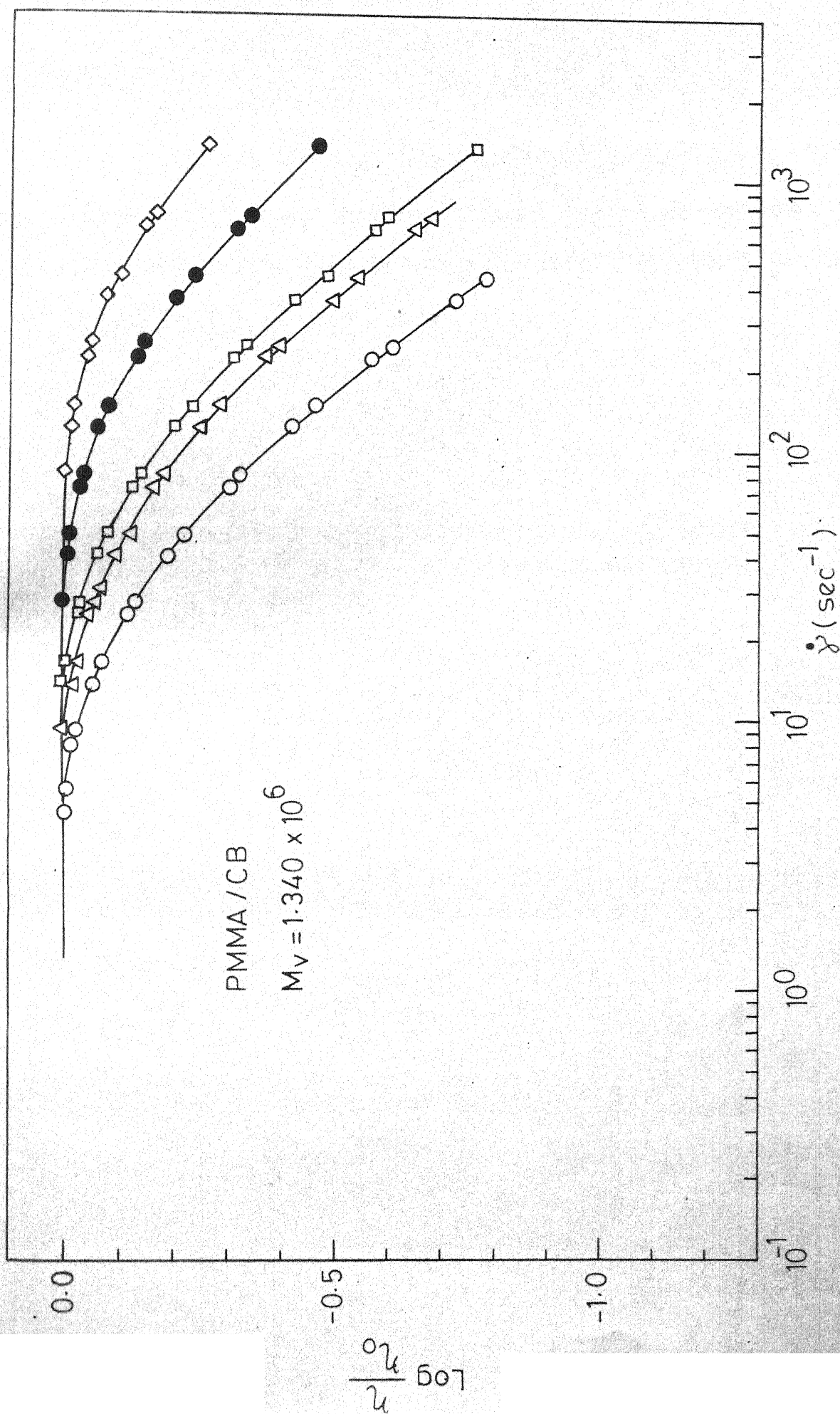


Fig.10 - $\text{Log } \frac{\eta}{\eta_0}$ versus $\dot{\gamma}$ for polymethylmethacrylate in Chlorobenzene (PMMA/CB) at 25°C. Chlorobenzene is a good solvent for this polymer ; $M_V = 1.340 \times 10^6$; The points represent different concentrations: (o) 11.00g/dl ; (Δ) 8.65 g/dl, (\square) 7.80g/dl ; (\bullet) 5.74 g/dl ; (\diamond) 3.98 g/dl

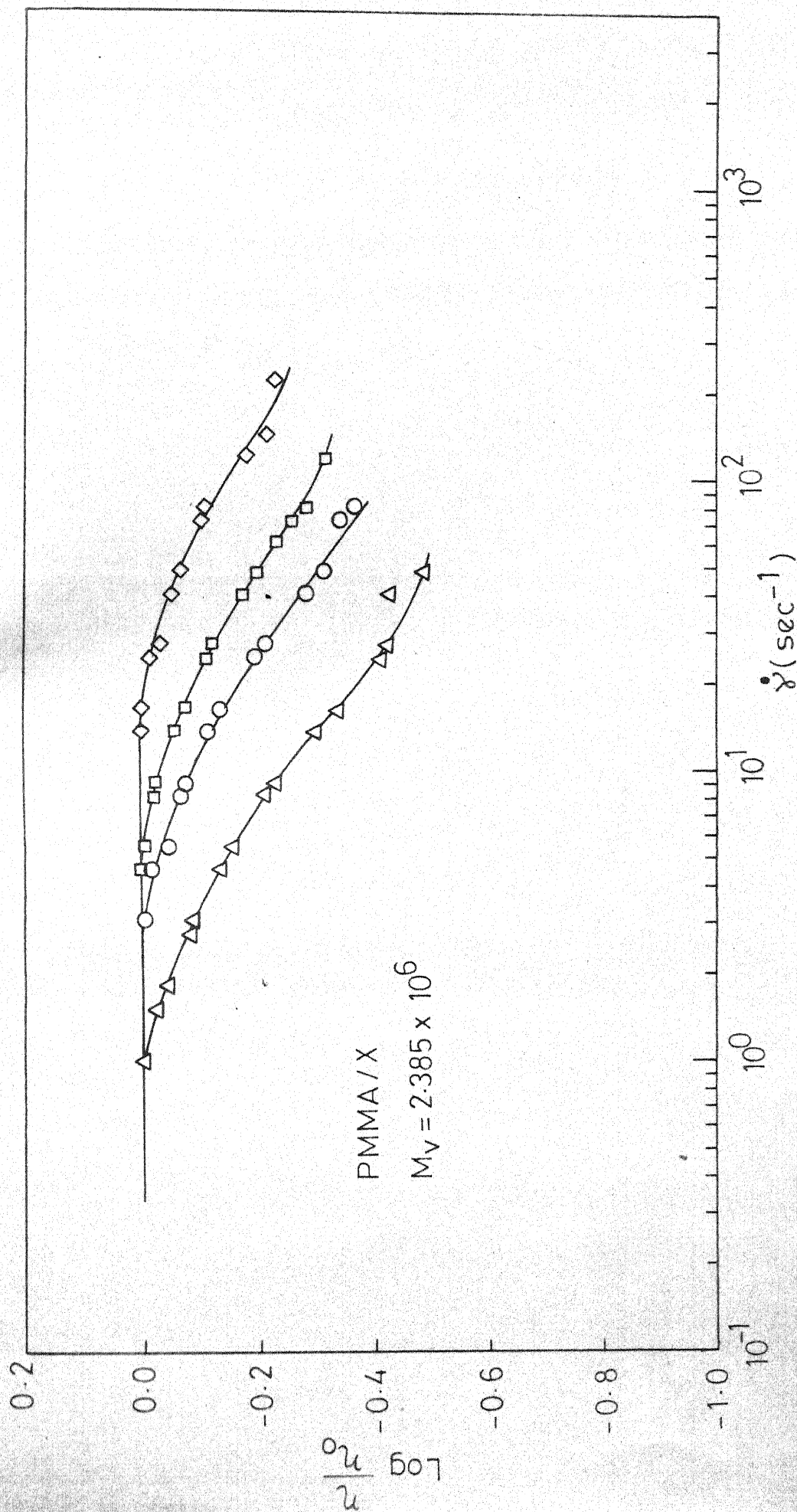


Fig. 11 - $\text{Log } \frac{\eta}{\eta_0}$ versus $\dot{\gamma}$ for polymethylmethacrylate in m-Xylene (PMMA/X) at 35°. m-Xylene is a poor solvent for this polar polymer $M_v = 2.385 \times 10^6$; The points represent different concentrations: (Δ) 4.92 g/dl, (o) 3.65 g/dl, (\square) 3.115 g/dl, (\diamond) 2.185 g/dl.

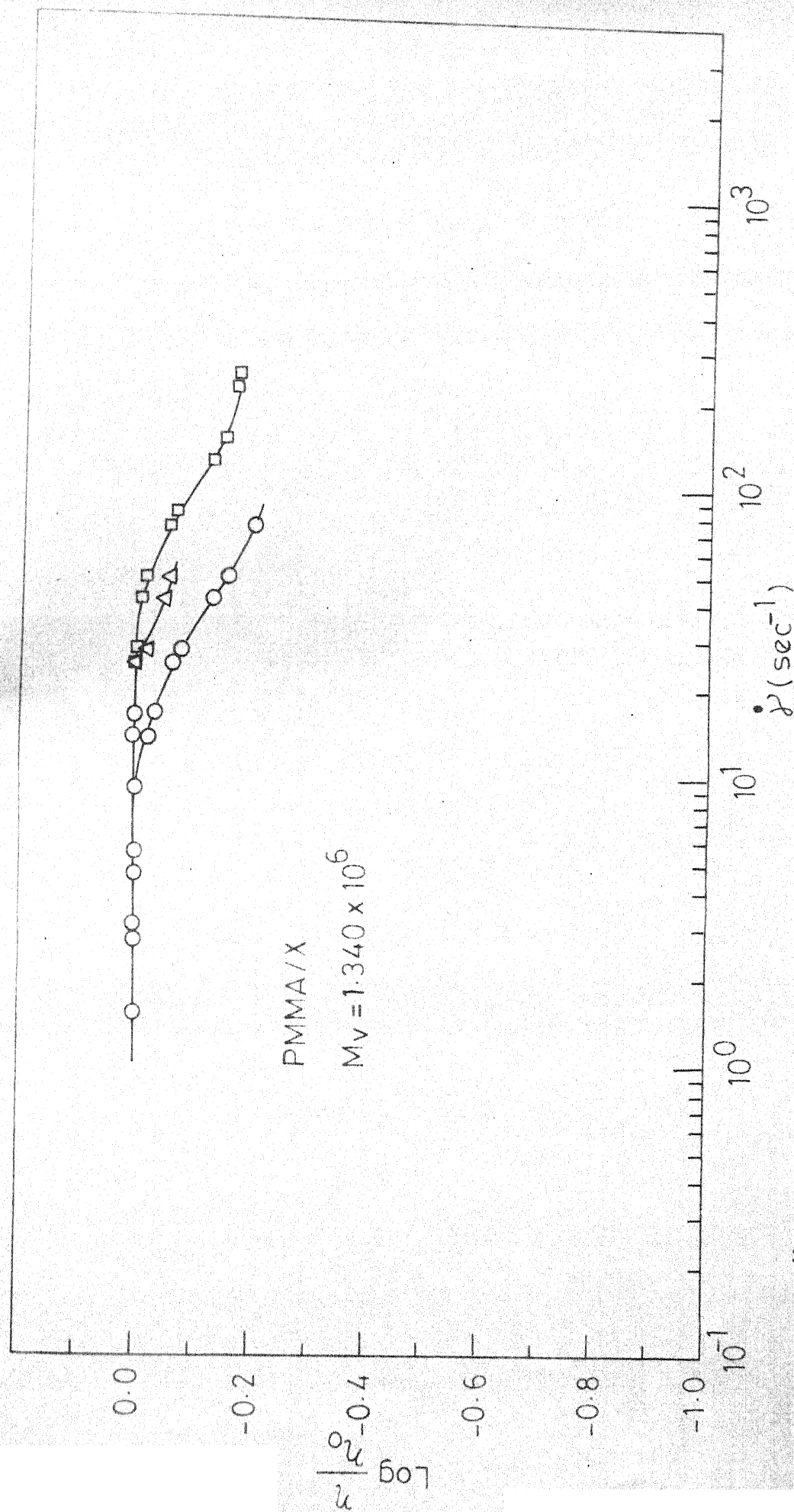


Fig. 12 - $\log \frac{\eta}{\eta_0}$ versus $\dot{\gamma}$ for polymethylmethacrylate in m-Xylene (poor solvent) at 35°C, $M_v = 1.340 \times 10^6$; The points represent different concentrations: (○) 3.5 g/dl; (Δ) 3.885 g/dl; (◻) 5.48 g/dl.

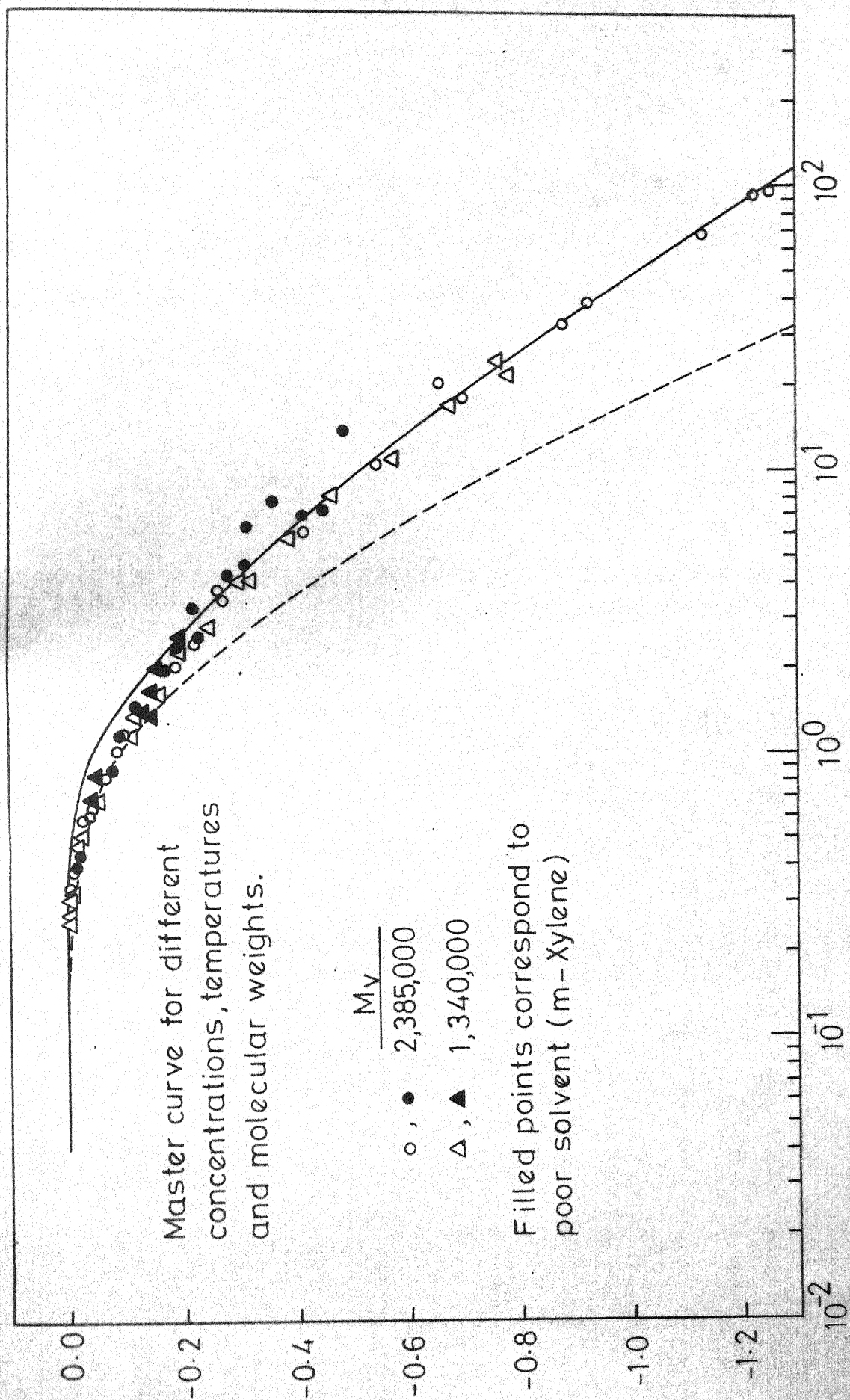


Fig.13 - Composite master curve for PMMA solutions. The dotted line is the best fit obtained using Williams theoretical master curve [3] and solid line is that of Graessley's master curve [22].

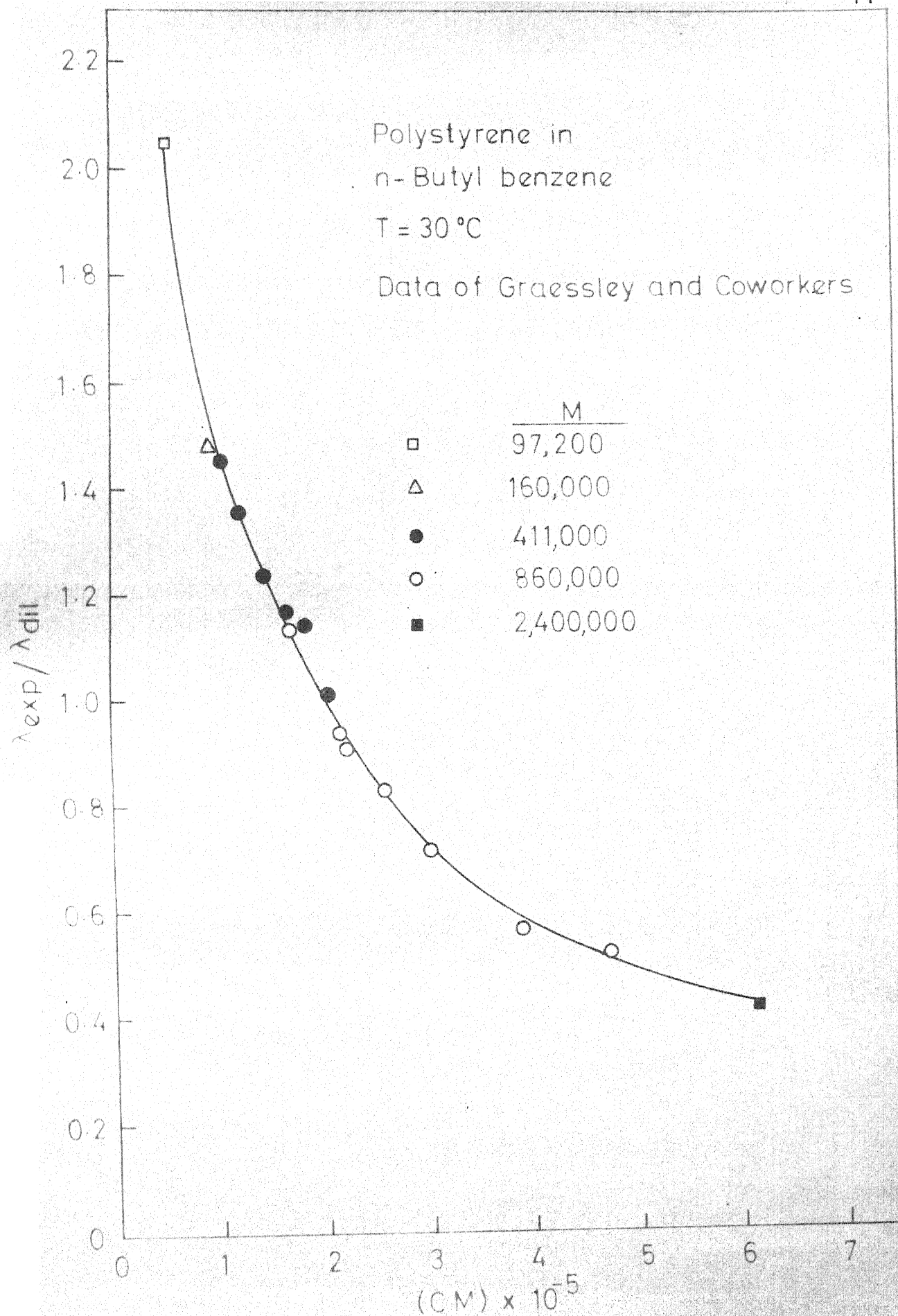


Fig 14 - λ_{dil} was calculated using Rouse equation.

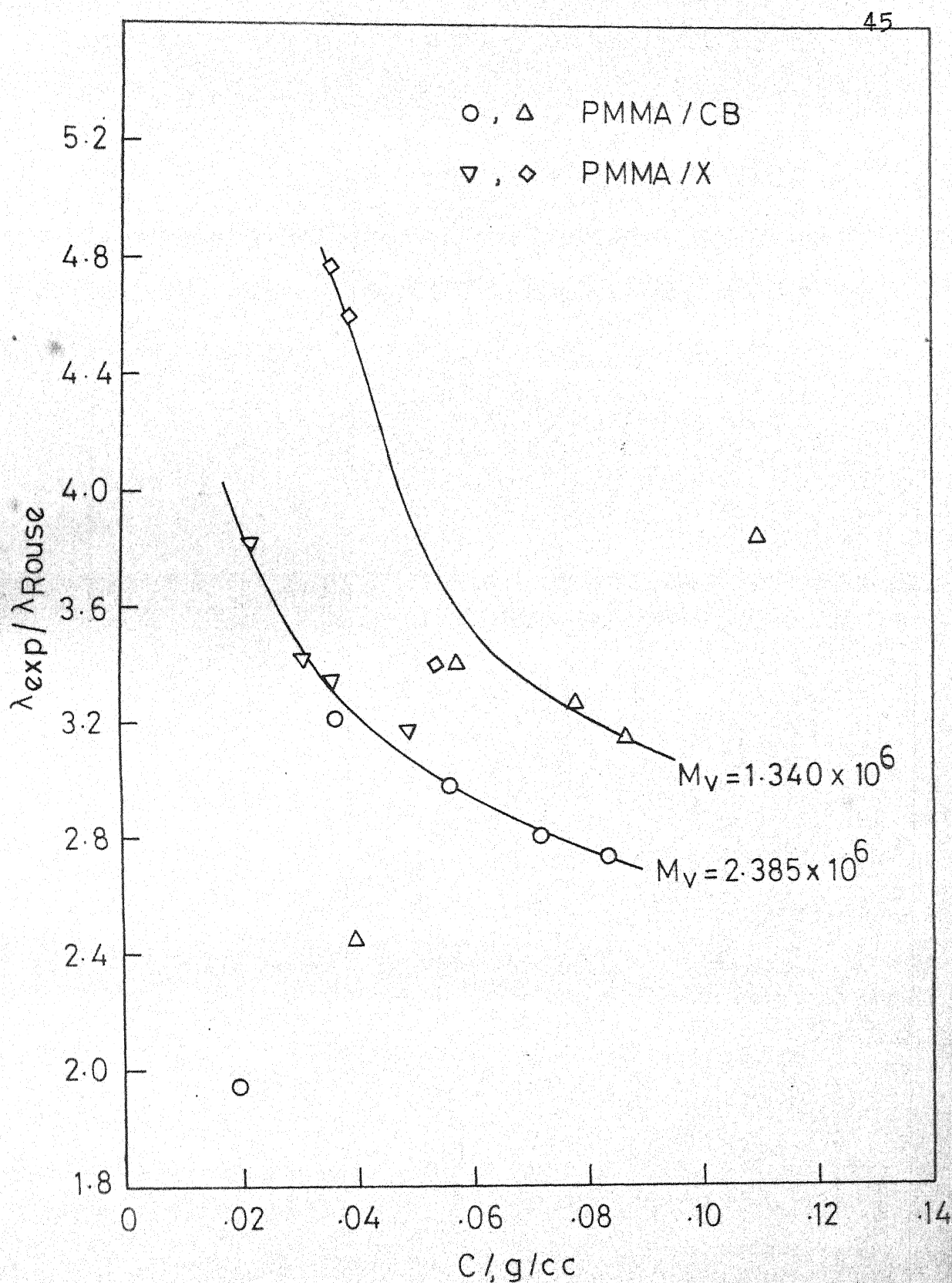


Fig.15-Ratio of experimental to theoretical relation time for different molecular weights of PMMA solutions in good (chlorobenzene) and poor (m-Xylene) solvent. The points represent different molecular weights: (○,▽) 2.385×10^6 ; (△,◇) 1.340×10^6 .

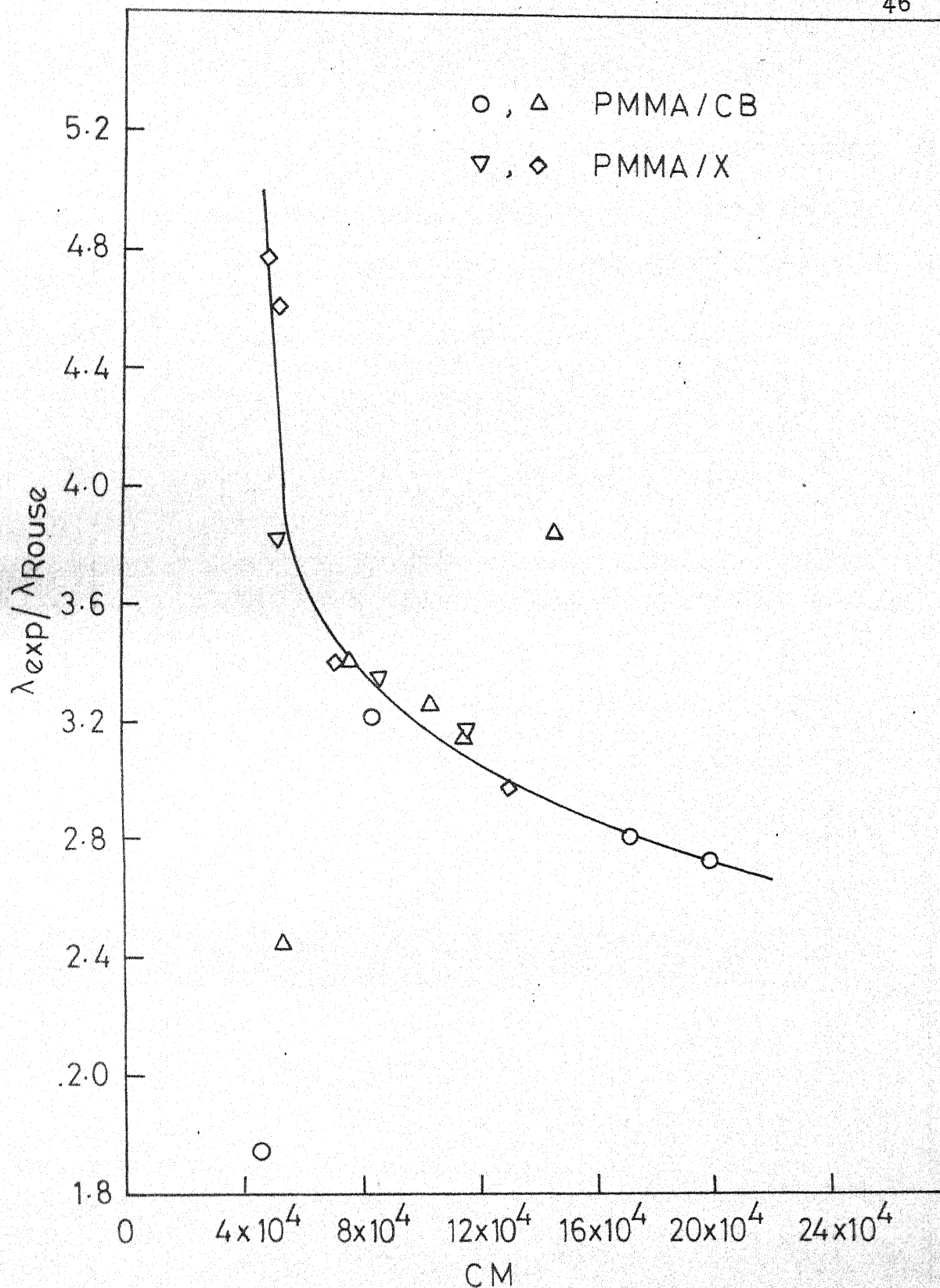


Fig.16 - Relaxation time ratio versus the product of molecular weight and concentration. The points correspond different molecular weights of PMMA solutions in good and poor solvents : (○,▽) 2.385×10^6 ; (△,◇) 1.340×10^6 .

APPENDIXTHEORETICAL MASTER CURVESBueche's Master Curve:

$\frac{\eta - \eta_s}{\eta_0 - \eta_s}$.997	.988	.847	.667	.526	.356	.261	.160
$\dot{\gamma} \lambda$.05	.10	.40	.70	1.0	2.0	4.0	10.0

Williams Master Curve for Concentrated Solutions:

$\frac{\eta - \eta_s}{\eta_0 - \eta_s}$.99	.98	.96	.80	.60	.50	.40	3.0
$\dot{\gamma} \lambda$.14	.20	.32	.99	1.88	2.57	3.60	5.1

Graessley's Entanglement Master Curve:

$\frac{\eta}{\eta_0}$.998	.961	.858	.714	.50	.261	.160	.083
$\dot{\gamma} \lambda$.20	.624	1.17	1.96	4.00	11.48	23.4	60.0

Density Data on Solutions Employed:

PMMA-CB

$$\text{Density} = 1.1 + 0.172 (W)$$

PMMA-X

$$\text{Density} = 0.864 / (1.0 - 0.2987 (W))$$

...

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VISCOSITY OF POLYMETHYLMETHACRYLATE

TEMPERATURE =25 C SOLVENT=CHLOROBENZENE
 CONCENTRATION= 0.08400GM/C.C MOLECULAR WEIGHT= 0.23850E 07

SHEAR RATE,1/SEC SHEAR STRESS,DYN/CM.CM VISCOSITY,POISE

0.500000E 00	0.579885E 02	0.115977E 03
0.900000E 00	0.104148E 03	0.115721E 03
0.100000E 01	0.117996E 03	0.117996E 03
0.150000E 01	0.170792E 03	0.113861E 03
0.180000E 01	0.200219E 03	0.111233E 03
0.270000E 01	0.284172E 03	0.105249E 03
0.300000E 01	0.310714E 03	0.103571E 03
0.450000E 01	0.422364E 03	0.938587E 02
0.540000E 01	0.482949E 03	0.894350E 02
0.810000E 01	0.640200E 03	0.790370E 02
0.900000E 01	0.669300E 03	0.743667E 02
0.135000E 02	0.855540E 03	0.633733E 02
0.162000E 02	0.954480E 03	0.589185E 02
0.240000E 02	0.116982E 04	0.481407E 02
0.270000E 02	0.119892E 04	0.444044E 02
0.405000E 02	0.146373E 04	0.361415E 02
0.486000E 02	0.156558E 04	0.322136E 02
0.729000E 02	0.179838E 04	0.246691E 02
0.810000E 02	0.186240E 04	0.229926E 02
0.121500E 03	0.209229E 04	0.172205E 02
0.145800E 03	0.219996E 04	0.150889E 02
0.218700E 03	0.242403E 04	0.110838E 02
0.243000E 03	0.249387E 04	0.102628E 02
0.437400E 03	0.282270E 04	0.645336E 01

VISCOSITY OF POLYMETHYLMETHACRYLATE

TEMPERATURE = 25 C SOLVENT = CHLORO BENZENE
 CONCENTRATION = 0.05660 GM/C.C MOLECULAR WEIGHT = 0.23850E 07

SHEAR RATE, 1/SEC SHEAR STRESS, DYN/CM.CM VISCOSITY, POISE

0.150000E 01	0.288470E 02	0.192313E 02
0.270000E 01	0.540485E 02	0.200180E 02
0.300000E 01	0.580110E 02	0.193370E 02
0.450000E 01	0.866995E 02	0.192666E 02
0.540000E 01	0.101123E 03	0.187265E 02
0.810000E 01	0.144552E 03	0.178459E 02
0.900000E 01	0.158500E 03	0.176111E 02
0.135000E 02	0.218254E 03	0.161670E 02
0.162000E 02	0.250271E 03	0.154489E 02
0.243000E 02	0.337050E 03	0.138704E 02
0.270000E 02	0.362730E 03	0.134344E 02
0.405000E 02	0.462240E 03	0.114133E 02
0.486000E 02	0.513600E 03	0.105679E 02
0.729000E 02	0.635580E 03	0.871852E 01
0.810000E 02	0.678915E 03	0.838167E 01
0.121500E 03	0.818550E 03	0.673704E 01
0.145800E 03	0.881145E 03	0.604352E 01
0.218700E 03	0.103041E 04	0.471152E 01
0.243000E 03	0.106893E 04	0.439889E 01
0.364500E 03	0.123264E 04	0.338173E 01
0.437400E 03	0.130005E 04	0.297222E 01
0.656000E 03	0.148944E 04	0.227049E 01
0.729000E 03	0.154080E 04	0.211358E 01
0.131200E 04	0.185859E 04	0.141661E 01

VISCOSITY OF POLYMETHYLMETHACRYLATE

TEMPERATURE = 25.0

CONCENTRATION = 0.03570 GM/CC

SOLVENT = CHLOROBENZENE

MOLECULAR WEIGHT = 0.23850E 07

SHEAR RATE, 1/SEC SHEAR STRESS, DYN/CM.CM VISCOSITY, POISE

0.150000E 01	0.158500E 01	0.105667E 01
0.270000E 01	0.586450E 01	0.217204E 01
0.300000E 01	0.697400E 01	0.232467E 01
0.450000E 01	0.125215E 02	0.278256E 01
0.540000E 01	0.152160E 02	0.281778E 01
0.810000E 01	0.248845E 02	0.307216E 01
0.900000E 01	0.258355E 02	0.287061E 01
0.135000E 02	0.396250E 02	0.293519E 01
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0.270000E 02	0.762385E 02	0.282365E 01
0.405000E 02	0.106987E 03	0.264167E 01
0.486000E 02	0.124105E 03	0.255361E 01
0.729000E 02	0.170229E 03	0.233510E 01
0.810000E 02	0.184177E 03	0.227379E 01
0.121500E 03	0.242505E 03	0.199593E 01
0.145800E 03	0.272303E 03	0.186765E 01
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0.243000E 03	0.378780E 03	0.155877E 01
0.364500E 03	0.465450E 03	0.127695E 01
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0.131200E 04	0.837810E 03	0.638575E 00

VISCOSITY OF POLYMETHYLMETHACRYLATE

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SHEAR RATE,1/SEC SHEAR STRESS,DYN/CM.CM VISCOSITY,POISE

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0.486000E 02	0.226655E 02	0.466368E 00
0.729000E 02	0.342360E 02	0.469630E 00
0.810000E 02	0.380400E 02	0.469630E 00
0.121500E 03	0.553165E 02	0.455280E 00
0.145800E 03	0.649850E 02	0.445713E 00
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0.243000E 03	0.998550E 02	0.410926E 00
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0.437400E 03	0.156598E 03	0.358020E 00
0.656000E 03	0.207952E 03	0.317000E 00
0.729000E 03	0.222217E 03	0.304824E 00
0.131200E 04	0.327420E 03	0.249558E 00

VISCOSITY OF POLYMETHYLMETHACRYLATE

TEMPERATURE =25 C SOLVENT=CHLOROBENZENE
 CONCENTRATION= 0.11000GM/C.C MOLECULAR WEIGHT= 0.13400E 07

SHEAR RATE,1/SEC SHEAR STRESS,DYN/CM.CM VISCOSITY,POISE

0.150000E 01	0.643510E 02	0.429007E 02
0.270000E 01	0.114120E 03	0.422667E 02
0.300000E 01	0.128543E 03	0.428478E 02
0.450000E 01	0.192419E 03	0.427598E 02
0.540000E 01	0.226655E 03	0.419731E 02
0.810000E 01	0.333840E 03	0.412148E 02
0.900000E 01	0.362730E 03	0.403033E 02
0.135000E 01	0.505575E 03	0.374500E 02
0.162000E 02	0.584220E 03	0.360630E 02
0.243000E 02	0.789660E 03	0.324963E 02
0.270000E 02	0.847440E 03	0.313867E 02
0.450000E 02	0.110263E 04	0.272256E 02
0.486000E 02	0.123264E 04	0.253630E 02
0.728900E 04	0.154561E 04	0.212048E 00
0.810000E 02	0.163228E 04	0.201517E 02
0.821500E 03	0.198057E 04	0.163010E 02
0.145800E 03	0.214749E 04	0.147290E 02
0.208700E 03	0.248614E 04	0.113678E 02
0.243000E 03	0.258084E 04	0.106207E 02
0.364500E 03	0.292752E 04	0.803160E 01
0.437400E 03	0.308320E 04	0.704894E 01

VISCOSITY OF POLYMETHYLMETHACRYLATE

TEMPERATURE = 25 C SOLVENT = CHLOROBENZENE
 CONCENTRATION = 0.08650 GM/C.C MOLECULAR WEIGHT = 0.13400E 07

SHEAR RATE, 1/SEC SHEAR STRESS, DYN/CM.CM VISCOSITY, POISE

0.150000E 01	0.282130E 02	0.188087E 02
0.270000E 01	0.515125E 02	0.190787E 02
0.300000E 01	0.573770E 02	0.191257E 02
0.450000E 01	0.871750E 02	0.193722E 02
0.540000E 01	0.105085E 03	0.194603E 02
0.810000E 01	0.155964E 03	0.192548E 02
0.900000E 01	0.173399E 03	0.192666E 02
0.135000E 02	0.252015E 03	0.186678E 02
0.162000E 02	0.296078E 03	0.182764E 02
0.243000E 02	0.422115E 03	0.173710E 02
0.270000E 02	0.457425E 03	0.169417E 02
0.405000E 02	0.630765E 03	0.155744E 02
0.486000E 02	0.722250E 03	0.148611E 02
0.729000E 02	0.969420E 03	0.132979E 02
0.810000E 02	0.102720E 04	0.126815E 02
0.121500E 03	0.131289E 04	0.108057E 02
0.145800E 03	0.146055E 04	0.100175E 02
0.218700E 03	0.181365E 04	0.829287E 01
0.243000E 03	0.190353E 04	0.783846E 01
0.364500E 03	0.225984E 04	0.619984E 01
0.437400E 03	0.243639E 04	0.557016E 01
0.656000E 03	0.283282E 04	0.431833E 01
0.729000E 03	0.294357E 04	0.403782E 01

VISCOSITY OF POLYMETHYLMETHACRYLATE

TEMPERATURE = 25 C SOLVENT=CHLOROBENZENE
 CONCENTRATION= 0.07800GM/C.C MOLECULAR WEIGHT= 0.13400E 07

SHEAR RATE, 1/SEC SHEAR STRESS, DYN/CM.CM VISCOSITY, POISE

0.150000E 01	0.182275E 02	0.121517E 02
0.270000E 01	0.348700E 02	0.129148E 02
0.300000E 01	0.383570E 02	0.127857E 02
0.450000E 01	0.607055E 02	0.134901E 02
0.540000E 01	0.721175E 02	0.133551E 02
0.810000E 01	0.108572E 03	0.134040E 02
0.900000E 01	0.120935E 03	0.134373E 02
0.135000E 02	0.180690E 03	0.133844E 02
0.162000E 02	0.213499E 03	0.131790E 02
0.243000E 02	0.304637E 03	0.125365E 02
0.270000E 02	0.335445E 03	0.124239E 02
0.405000E 02	0.465450E 03	0.114926E 02
0.486000E 02	0.537675E 03	0.110633E 02
0.729000E 02	0.727065E 03	0.997346E 01
0.810000E 02	0.783240E 03	0.966963E 01
0.121500E 03	0.102559E 04	0.844111E 01
0.145800E 03	0.113634E 04	0.779383E 01
0.218700E 03	0.143808E 04	0.657558E 01
0.243000E 03	0.151191E 04	0.622185E 01
0.364500E 03	0.185859E 04	0.509901E 01
0.437400E 03	0.201588E 04	0.460878E 01
0.656000E 03	0.236095E 04	0.359902E 01
0.729000E 03	0.244602E 04	0.335531E 01
0.131200E 04	0.299172E 04	0.228027E 01

VISCOSITY OF POLYMETHYLMETHACRYLATE

TEMPERATURE = 25 C SOLVENT=CHLOROBENZENE
 CONCENTRATION= 0.5740GM/C.C MOLECULAR WEIGHT= 0.13400E 07

SHEAR RATE, 1/SEC SHEAR STRESS, DYN/CM.CM VISCOSITY, POISE

0.150000E 01	0.253600E 01	0.169067E 01
0.270000E 01	0.649850E 01	0.240685E 01
0.300000E 01	0.713250E 01	0.237750E 01
0.450000E 01	0.131555E 02	0.292344E 01
0.540000E 01	0.164840E 02	0.305259E 01
0.810000E 01	0.267865E 02	0.330698E 01
0.900000E 01	0.304320E 02	0.338133E 01
0.135000E 02	0.459650E 02	0.340481E 01
0.162000E 02	0.554750E 02	0.342438E 01
0.243000E 02	0.843220E 02	0.347004E 01
0.270000E 02	0.931980E 02	0.345178E 01
0.405000E 02	0.137419E 03	0.339307E 01
0.486000E 02	0.163730E 03	0.336894E 01
0.729000E 02	0.234580E 03	0.321783E 01
0.810000E 02	0.257245E 03	0.317587E 01
0.121500E 03	0.362730E 03	0.298543E 01
0.145800E 03	0.417300E 03	0.286214E 01
0.218700E 03	0.553725E 03	0.253189E 01
0.243000E 03	0.605085E 03	0.249006E 01
0.364500E 03	0.786450E 03	0.215761E 01
0.437400E 03	0.873120E 03	0.199616E 01
0.656000E 03	0.109821E 04	0.167106E 01
0.729000E 03	0.115399E 04	0.158298E 01
0.131200E 04	0.154722E 04	0.117928E 01

VISCOSITY OF POLYMETHYLMETHACRYLATE

TEMPERATURE = 25 C

SOLVENT = CHLOROBENZENE

CONCENTRATION = 0.03990 GM/C.C

MOLECULAR WEIGHT = 0.13400E 07

SHEAR RATE, 1/SEC SHEAR STRESS, DYN/CM.CM VISCOSITY, POISE

0.810000E 01	0.649850E 01	0.802284E 00
0.900000E 01	0.697400E 01	0.774889E 00
0.135000E 02	0.133140E 02	0.986222E 00
0.162000E 02	0.156915E 02	0.968611E 00
0.243000E 02	0.258355E 02	0.106319E 01
0.270000E 02	0.285300E 02	0.105667E 01
0.405000E 02	0.437460E 02	0.108015E 01
0.486000E 02	0.535730E 02	0.110233E 01
0.729000E 02	0.795670E 02	0.109145E 01
0.810000E 02	0.884430E 02	0.109189E 01
0.121500E 03	0.128860E 03	0.106058E 01
0.145800E 03	0.152794E 03	0.104797E 01
0.218700E 03	0.218888E 03	0.100086E 01
0.243000E 03	0.238384E 03	0.981004E 00
0.364500E 03	0.322605E 03	0.885062E 00
0.437400E 03	0.378780E 03	0.865981E 00
0.656000E 03	0.511995E 03	0.780480E 00
0.729000E 03	0.542490E 03	0.744156E 00
0.131200E 04	0.786450E 03	0.599428E 00

VISCOSITY OF POLYMETHYLMETHACRYLATE

TEMPERATURE =35 C SOLVENT=M-XYLENE
 CONCENTRATION= 0.04920GM/C.C MOLECULAR WEIGHT= 0.23850E 07

SHEAR RATE,1/SEC SHEAR STRESS,DYN/CM.CM VISCOSITY,POISE

0.500000E 00	0.392360E 02	0.784720E 02
0.900000E 00	0.675090E 02	0.750100E 02
0.100000E 01	0.773180E 02	0.773180E 02
0.150000E 01	0.109630E 03	0.730867E 02
0.180000E 01	0.126363E 03	0.702017E 02
0.270000E 01	0.174831E 03	0.647522E 02
0.300000E 01	0.190410E 03	0.634700E 02
0.450000E 01	0.255034E 03	0.566742E 02
0.540000E 01	0.293693E 03	0.543876E 02
0.810000E 01	0.384282E 03	0.474422E 02
0.900000E 01	0.408516E 03	0.453907E 02
0.135000E 02	0.518146E 03	0.383812E 02
0.162000E 02	0.570076E 03	0.351899E 02
0.243000E 02	0.727500E 03	0.299383E 02
0.270000E 02	0.803160E 03	0.297467E 02
0.405000E 02	0.100104E 04	0.247170E 02
0.486000E 02	0.123384E 04	0.253877E 02

VISCOSITY OF POLYMETHYLMETHACRYLATE

TEMPERATURE =35 C SOLVENT=M-XYLENE
 CONCENTRATION= 0.03650GM/C.C MOLECULAR WEIGHT= 0.23850E 07

SHEAR RATE,1/SEC SHEAR STRESS,DYN/CM.CM VISCOSITY,POISE

0.150000E 01	0.278960E 02	0.185973E 02
0.270000E 01	0.485010E 02	0.179633E 02
0.300000E 01	0.554750E 02	0.184917E 02
0.450000E 01	0.795670E 02	0.176816E 02
0.540000E 01	0.925640E 02	0.171415E 02
0.810000E 01	0.127434E 03	0.157326E 02
0.900000E 01	0.139797E 03	0.155330E 02
0.135000E 02	0.191785E 03	0.142063E 02
0.162000E 02	0.218096E 03	0.134627E 02
0.243000E 02	0.285300E 03	0.117407E 02
0.270000E 02	0.305905E 03	0.113298E 02
0.405000E 02	0.391620E 03	0.966963E 01
0.486000E 02	0.436560E 03	0.898272E 01
0.729000E 02	0.616320E 03	0.845432E 01
0.810000E 02	0.648420E 03	0.800519E 01

VISCOSITY OF POLYMETHYLMETHACRYLATE

TEMPERATURE = 35 C

SOLVENT=M-XYLENE

CONCENTRATION= 0.0312 GM/C.C

MOLECULAR WEIGHT= 0.23850E 07

SHEAR RATE, 1/SEC SHEAR STRESS, DYN/CM.CM VISCOSITY, POISE

0.150000E 01	0.133140E 02	0.887600E 01
0.270000E 01	0.228240E 02	0.845333E 01
0.300000E 01	0.256770E 02	0.855900E 01
0.450000E 01	0.386740E 02	0.859422E 01
0.540000E 01	0.453310E 02	0.839463E 01
0.810000E 01	0.653020E 02	0.806198E 01
0.900000E 01	0.722760E 02	0.803067E 01
0.135000E 02	0.100172E 03	0.742015E 01
0.162000E 02	0.115071E 03	0.710315E 01
0.243000E 02	0.158817E 03	0.653568E 01
0.270000E 02	0.172765E 03	0.639870E 01
0.405000E 02	0.231410E 03	0.571383E 01
0.486000E 02	0.262476E 03	0.540074E 01
0.729000E 02	0.343470E 03	0.471152E 01
0.810000E 02	0.359520E 03	0.443852E 01
0.121500E 03	0.497550E 03	0.409506E 01

VISCOSITY OF POLYMETHYLMETHACRYLATE

TEMPERATURE =35 C SOLVENT=M-XYLENE
 CONCENTRATION= 0.2190GM/C.C MOLECULAR WEIGHT= 0.23850E 07

SHEAR RATE,1/SEC SHEAR STRESS,DYN/CM.CM VISCOSITY,POISE

0.300000E 01	0.221900E 01	0.739667E 00
0.450000E 01	0.412100E 01	0.915778E 00
0.540000E 01	0.697400E 01	0.129148E 01
0.810000E 01	0.120460E 02	0.148716E 01
0.900000E 01	0.126800E 02	0.140889E 01
0.135000E 02	0.215560E 02	0.159674E 01
0.162000E 02	0.259940E 02	0.160457E 01
0.243000E 02	0.374060E 02	0.153934E 01
0.270000E 02	0.399420E 02	0.147933E 01
0.405000E 02	0.576940E 02	0.142454E 01
0.486000E 02	0.672040E 02	0.138280E 01
0.729000E 02	0.928810E 02	0.127409E 01
0.810000E 02	0.100806E 03	0.124452E 01
0.121500E 03	0.129336E 03	0.106449E 01
0.145800E 03	0.141699E 03	0.971872E 00
0.218700E 03	0.209220E 03	0.956653E 00

VISCOSITY OF POLYMETHYLMETHACRYLATE

TEMPERATURE =35 C SOLVENT=M-XYLENE
 CONCENTRATION= 0.05400GM/C.C MOLECULAR WEIGHT= 0.13400E 07

SHEAR RATE,1/SEC SHEAR STRESS,DYN/CM.CM VISCOSITY,POISE

0.150000E 01	0.225070E 02	0.150047E 02
0.270000E 01	0.459650E 02	0.170241E 02
0.300000E 01	0.526220E 02	0.175407E 02
0.450000E 01	0.767140E 02	0.170476E 02
0.540000E 01	0.919300E 02	0.170241E 02
0.810000E 01	0.134725E 03	0.166327E 02
0.900000E 01	0.153111E 03	0.170123E 02
0.135000E 02	0.219364E 03	0.162492E 02
0.162000E 02	0.253600E 03	0.156543E 02
0.243000E 02	0.359520E 03	0.147951E 02
0.270000E 02	0.385200E 03	0.142667E 02
0.405000E 02	0.507180E 03	0.125230E 02
0.486000E 02	0.574590E 03	0.118228E 02
0.729000E 02	0.770400E 03	0.105679E 02

VISCOSITY OF POLYMETHYLMETHACRYLATE

TEMPERATURE =35 C SOLVENT=M-XYLENE
 CONCENTRATION= C.03890GM/C.C MOLECULAR WEIGHT= 0.13400E 07

SHEAR RATE,1/SEC SHEAR STRESS,DYN/CM.CM VISCOSITY,POISE

0.450000E 01	0.152160E 02	0.338133E 01
0.540000E 01	0.180690E 02	0.334611E 01
0.810000E 01	0.278960E 02	0.344395E 01
0.900000E 01	0.320170E 02	0.355744E 01
0.135000E 02	0.475500E 02	0.352222E 01
0.162000E 02	0.570600E 02	0.352222E 01
0.243000E 02	0.830540E 02	0.341786E 01
0.270000E 02	0.909790E 02	0.336959E 01
0.405000E 02	0.128385E 03	0.317000E 01
0.486000E 02	0.150575E 03	0.309825E 01
0.729000E 02	0.206050E 03	0.282647E 01
0.810000E 02	0.217145E 03	0.268080E 01
0.121500E 03	0.285300E 03	0.234815E 01
0.145800E 03	0.327420E 03	0.224568E 01

VISCOSITY OF POLYMETHYLMETHACRYLATE

TEMPERATURE = 35 C SOLVENT = M-XYLENE
 CONCENTRATION = 0.03580GM/C.C MOLECULAR WEIGHT = 0.13400E 07

SHEAR RATE, 1/SEC SHEAR STRESS, DYN/CM.CM VISCOSITY, POISE

0.270000E 01	0.317000E 01	0.117407E 01
0.300000E 01	0.412100E 01	0.137367E 01
0.450000E 01	0.729100E 01	0.162022E 01
0.540000E 01	0.120460E 02	0.223074E 01
0.810000E 01	0.164840E 02	0.203506E 01
0.900000E 01	0.196540E 02	0.218378E 01
0.135000E 02	0.310660E 02	0.230119E 01
0.162000E 02	0.358210E 02	0.221117E 01
0.243000E 02	0.545240E 02	0.224379E 01
0.270000E 02	0.586450E 02	0.217204E 01
0.405000E 02	0.859070E 02	0.212116E 01
0.486000E 02	0.101757E 03	0.209377E 01
0.729000E 02	0.141382E 03	0.193940E 01
0.810000E 02	0.152794E 03	0.188635E 01
0.121500E 03	0.201295E 03	0.165675E 01
0.145800E 03	0.225704E 03	0.154804E 01
0.218700E 03	0.327420E 03	0.149712E 01
0.243000E 03	0.362730E 03	0.149272E 01